chapter

12 Explaining Chemical Changes

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It is part of human nature to try to make sense of the world around us and to develop technologies to solve practical problems, especially problems involving survival in a harsh environment. Fire is one of the earliest technologies, and a good example of the many energy changes that are an important part of the natural world. What is fire, and how can it be used? Almost every culture has had its stories or explanations about the origin and use of fire. From the Greek culture we have the story of Prometheus, and from North American Aboriginal peoples there is the story of the coyote stealing fire from the fire beings to give to the humans. Western science also has its "fire story" in the form of theories of chemical reactions, such as combustion. Scientists have considerable empirical knowledge of fire, or combustion. They can take measurements and calculate the energy changes, and represent them quantitatively in various forms as shown in the previous chapter. How does fire, or any other reaction, get started? How does it progress? And how can it be manipulated to alter its rate? The answers to these questions form part of Western science's story or theory of fire and other reactions. This chapter will start to answer these questions.

Not surprisingly, the empirical and theoretical descriptions about the nature of chemical energy changes are interwoven with the technologies of energy changes. Technologies that are researched and developed lead to advances in science, and scientific research leads to improved technologies. An important example is the study and application of catalysts—substances used extensively to increase the rate of chemical reactions. Industries that use catalysts include oil refining (catalytic cracking), petrochemical production (for polymerization), and chemical technologies (such as automobile catalytic converters, **Figure 1**). The story or theory of chemical energy changes in this chapter will also include numerous important technological applications.

STARTING Points

Answer these questions as best you can with your current knowledge. Then, using the concepts and skills you have learned, you will revise your answers at the end of the chapter.

1. What is necessary for a successful collision to occur between reacting entities?
2. How do bond energies affect the rate and enthalpy of reaction?
3. (a) What is the purpose of using a catalyst in a chemical process?
   (b) Why does a catalyst have this effect?
4. List some technological products and processes that employ catalysts.

Career Connection:
Field Production Operator

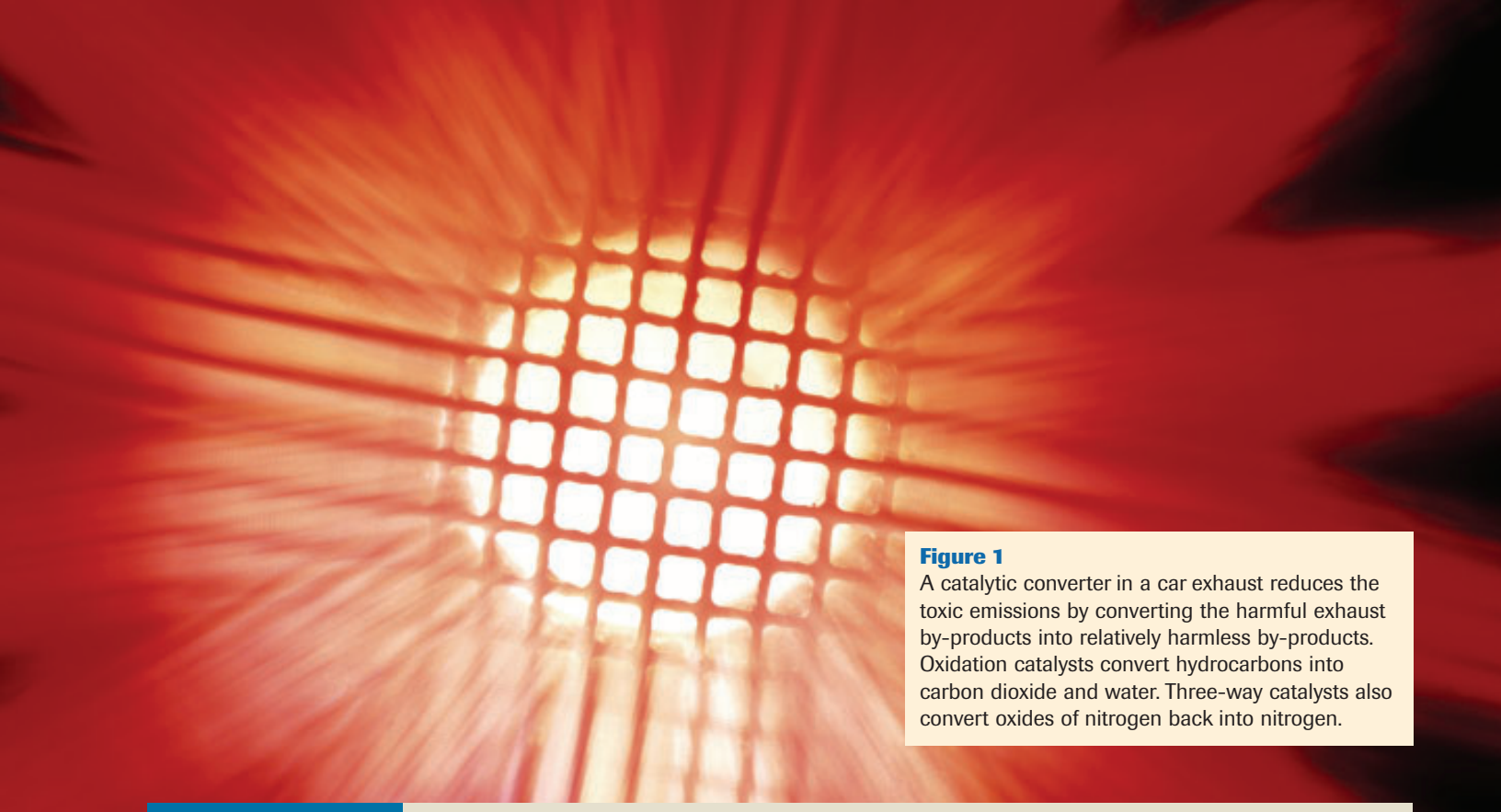

Figure 1
A catalytic converter in a car exhaust reduces the toxic emissions by converting the harmful exhaust by-products into relatively harmless by-products. Oxidation catalysts convert hydrocarbons into carbon dioxide and water. Three-way catalysts also convert oxides of nitrogen back into nitrogen.

Exploration Starting, Comparing, and Altering Reactions

We have seen many chemical reactions and know that they can be classified into different categories (reaction types). We can use this knowledge for predicting reaction equations and analyzing the stoichiometry of reactions. Although this is an important starting point, it leaves many questions unanswered. How do reactions start, and why do they keep going? Why do apparently similar reactions proceed at very different rates? How can the rate of a reaction be altered? The three parts of this Exploration will help you think about answers to these three questions.

Materials: eye protection; lab apron; 5 small test tubes; test tube rack; tweezers; distilled water wash bottle; 1 mol/L HCl(aq); 3% H_2O_2(aq); pieces of Mg(s), Zn(s), Fe(s), and fruits such as bananas and apples; some flakes of rust; cut open D cell

Hydrochloric acid is corrosive; hydrogen peroxide is both corrosive and a strong oxidizer. The chemicals in an open dry cell are likely to be corrosive and possibly toxic. Handle all substances with care. If they contact the skin, wash thoroughly with cool water. If they contact the eyes, flush with cool water for at least 15 min and inform your teacher.

Part A: Starting Reactions

Baking generally starts with measuring and mixing the ingredients, which include some potential reactants.

(a) Is mixing the ingredients all that you need to do? What is the usual next step in the baking procedure?

(b) List some observations that would indicate that a chemical reaction is occurring or has occurred.

When using a laboratory burner, natural gas and air are mixed together at the bottom of the tube and emerge out the top.

(c) Does the combustion start when the two reactants mix? What needs to be done next?

(d) List some observations that would indicate that a chemical reaction is occurring.

Part B: Comparing Reactions

One of the empirical properties of acids is that they react with active metals to produce hydrogen gas.

(e) When comparing the reactions of different metals with an acid, what variables need to be kept constant?

- Set up three test tubes containing about 1 cm depth of hydrochloric acid. Add a piece of Mg(s) to the first test tube, Zn(s) to the second, and Fe(s) to the third. Observe for a few minutes, and remove the metal with tweezers.

(f) List the similarities and differences in the evidence for the reactions of the three metals.

Part C: Altering Reactions

Hydrogen peroxide is produced in both natural and technological systems. When hydrogen peroxide decomposes it produces oxygen gas and water.

- Set up several clean test tubes with equal volumes (about 1 cm depth) of hydrogen peroxide.
- To all but one of the test tubes containing the hydrogen peroxide, add a small quantity of MnO_2(s) from the inside of a dry cell, some rust particles, or some small pieces of fruit. Leave one test tube containing only hydrogen peroxide.

(g) Record the evidence of reaction including comparisons of different test tubes.

(h) Why was one test tube set up with only hydrogen peroxide?

12.1 Activation Energy

Learning Tip

When using the stoichiometric law to make predictions, we normally assume that the chemical reaction in question is
- quantitative (reacts 100%)
- spontaneous (happens without the input of energy)
- stoichiometric (has a fixed ratio)
- fast (reacts rapidly)

Chemical technologies, like most technologies, are evaluated on the basis of whether they are simple, economical, reliable, and efficient. Chemists, chemical engineers, and chemical technologists work on chemical processes for years—sometimes even decades—to perfect a technology that meets these criteria. Each chemical process, past and present, has its own story of people and technologies. For example, the refining of crude oil has changed significantly over the years, as has the design of automobile engines that use the gasoline refined from the crude oil. This chapter tells some of the inside stories of how chemists explain chemical reactions and how chemical engineers use and control chemical reactions.

Reaction Progress

From your own experience, including the Exploration on page 523, you can see that some reactions do not proceed spontaneously at room temperature unless additional energy is added to start them off. A lit match, for example, is needed to start the combustion of candle wax in a candle, wood in a campfire, and propane in a barbeque. Consider a thought experiment for a dangerous situation in which methane gas is escaping into a closed room and is mixing with the air. Based on what you know about methane and oxygen, the predicted reaction is highly exothermic. Why is this highly exothermic reaction not spontaneous—why does an immediate reaction not occur to form the more thermally stable products carbon dioxide and water? A spark from a light switch being turned on, however, can cause an explosive reaction of the methane–air mixture. Why is this initiating energy source necessary to cause the reaction?

From your experience and from the Exploration, you may also have noticed that different reactants appear to react at different rates, even when all other variables are controlled. Why does changing one of the reactants in a similar chemical reaction make such a difference in the rate of the reaction? For example, different metals in contact with the same acid react at varying rates, and the same metal in contact with different acids reacts at varying rates. Consider another thought experiment where the flame of a propane torch is applied for the same period of time to different types of wood cut into identical shavings. In this case, the initiating energy is the same; however, the resulting rates of reaction are different. Some of the wood shavings burn very quickly while others burn very slowly. What is there about the different wood shavings that produces a varying rate of reaction? How can we explain this phenomenon?

Some reactants have different temperatures at which they start reacting. Also, some reactants at the same temperature react at different rates. What theoretical explanation is there for the different ignition temperatures and for the varying rates of reaction for different reactants?

DID YOU KNOW ?

Thought Experiments

Chemists can communicate evidence in a number of ways, one being by a thought experiment. Thought experiments are done in the mind. With prompting, we visualize the design, materials, procedure, and evidence collection, although no actual experiment is carried out.

DID YOU KNOW ?

Rate of Reaction

As you may have learned in past courses, there is evidence to show that the rate of a chemical reaction is generally increased by
- increasing the temperature
- increasing the pressure of a gas
- increasing the surface area of a liquid or solid
- changing one of the reactants
- adding a catalyst

Collision–Reaction Theory

Although empirical knowledge is the foundation of science, an ultimate aim of science is to understand processes by creating simple, consistent, and logical theories. Scientists develop theoretical knowledge, and communicate it by way of models and analogies. They test the resultant knowledge by judging its ability to describe, explain, and predict. Theories are often better at explaining than at predicting. The collision–reaction theory is an excellent example of this type of theory. It is easier to explain reactions using the theory than it is to make predictions of specific reactions.

Chemists created the collision–reaction theory to describe, explain, and predict characteristics of chemical reactions. Some of the main ideas of the collision–reaction theory are the following:

- A chemical sample consists of entities (atoms, ions, or molecules) that are in constant random motion at various speeds, rebounding elastically from collisions with each other. (Kinetic energy is conserved during elastic collisions.)
- A chemical reaction must involve collisions of reactant entities.
- An effective collision requires sufficient energy. Collisions with the required minimum energy have the potential to react.
- An effective collision also requires the correct orientation (positioning) of the colliding entities so that bonds can be broken and new bonds formed.
- Ineffective collisions involve entities that rebound elastically from the collision.

When looking at different reactions, chemists have noticed that some reactions appear to occur more readily than others. According to collision–reaction theory, reactions can only take place when entities collide, but not all collisions result in a reaction. If the orientation is correct and the energy is sufficient, then a reaction can occur (**Figure 1**). In other reactions, however, the collisions of reactant entities may involve insufficient energy or the collision may not have the correct orientation (**Figure 2**).

To use the collision–reaction theory more effectively, we need to consider other factors, such as the nature of the bonds present and the type of reaction occurring.

DID YOU KNOW?

Reaction Kinetics

In May 1884, Svante Arrhenius presented his doctoral thesis on a theory of ionic dissociation. His study jump-started branches of chemistry called *physical chemistry* and *reaction kinetics*. However, it wasn't until the 1920s and 1930s that these topics became part of organic chemistry, until the 1940s and 1950s for inorganic chemistry, and, finally, completing the reform, into high school chemistry textbooks in the 1960s.

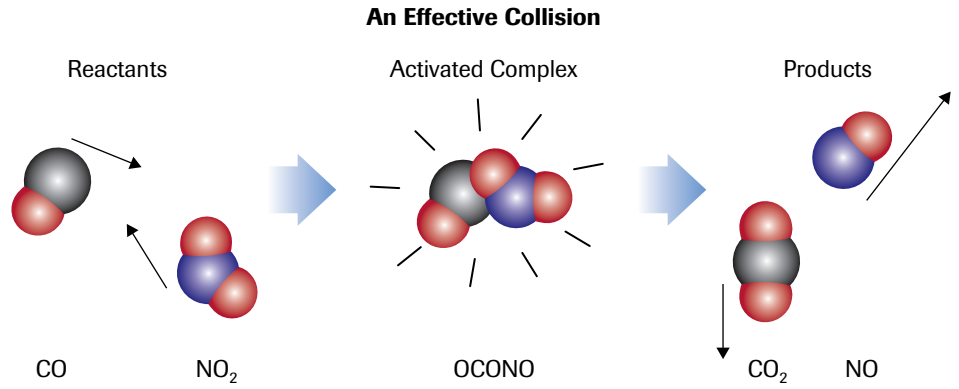

Figure 1
These molecules have both the correct orientation and sufficient energy, so the collision is effective: the atoms are rearranged and products are formed.

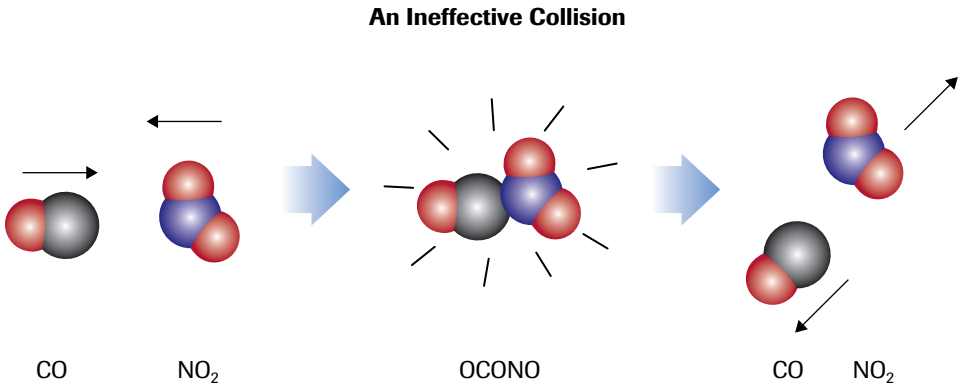

Figure 2
These molecules collide with a "wrong" orientation, so the bonds do not rearrange and no new substances form. The collision is ineffective.

BIOLOGY CONNECTION

"Cold-Blooded" Animals?

Many biological reactions take place at around 37 °C. How, then, do cold-blooded animals manage to live and function, despite being cooler than this? In your Biology course, you may discover that cold-blooded animals aren't always quite as cold as we think.

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In summary, there are two sources of evidence that need explaining. First, why do some chemicals react faster than others, when all other variables except the type of chemical are controlled (for example, why does magnesium react faster than zinc with hydrochloric acid)? Second, why do some reactions require an initial input of external energy to react (for example, why is a match needed to start the combustion of a hydrocarbon)? Empirical chemists gather the evidence and establish empirical concepts, such as generalizations about reaction rates. Theoretical chemists create explanations for the evidence gathered by the empirical chemists. The empirical and theoretical chemists may work as a team in the same university or may be around the world from each other. Likewise, the theory might be developed ahead of the evidence. The empirical chemist may have the role of testing the theory created by the theoretician. So what concepts did the theoretical chemists come up with?

WWW WEB Activity

Simulation—Collisions and Reactions

View the animations to see models of effective and ineffective collisions. Draw models to represent the orientation of the atoms for both types of collision.

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Practice

1. What two conditions must be met for two molecules to react?
2. Provide one scientific reason and one technological reason for understanding how chemical reactions occur.
3. Consider a thought experiment in which nitrogen and oxygen gases are mixed, as in air. No spontaneous reaction occurs under normal conditions or even by supplying high temperature and pressure. Then consider a lightning strike, which provides evidence for the production of nitrogen oxides. The evidence for this reaction is so strong that scientists list this reaction as part of the nitrogen cycle.
   (a) Write a balanced chemical equation for the reaction of nitrogen and oxygen to produce nitrogen dioxide, including the enthalpy change.
   (b) Draw and label a chemical potential energy diagram to express the enthalpy change for this reaction.
   (c) Create a hypothesis to explain why lightning is necessary to initiate this reaction.

DID YOU KNOW ?

Creating a Concept

Svante Arrhenius, in 1889, created the theoretical concept of activation energy to explain his laboratory work involving the effect of temperature on rates of reaction. This followed his theory of ionic dissociation (1884) and preceded his hypothesis that carbon dioxide variations in the atmosphere may have caused the extinction of dinosaurs and the advent of ice ages. Of course, you know about his contributions to acid–base theory.

Activation Energy of a Reaction

Since empirically measured reaction rates are often relatively slow, and in many cases too slow to be detectable (as in the nitrogen–oxygen reaction of air), chemists are forced to interpret the evidence as showing that normally only an extremely tiny fraction of the collisions actually produce products. The theoretical explanation for this evidence involves the concept of **activation energy**—an energy barrier that must be overcome for a chemical reaction to occur. Entities must reach this minimum energy before they can react. The input energy (which supplies the activation energy) may be in the form of heat, light, or electricity.

The concept of chemical activation energy, E_a, can be illustrated by an analogy with gravitational potential energy. Consider the analogy of a billiard ball rolling on a smooth

track shaped as shown in **Figure 3**. The ball leaves point A moving to the right. As it travels on the uphill portion of the track it slows down—as kinetic energy is converted to gravitational potential energy. The ball can only successfully overcome the rise of the track to reach point B if it has a large enough initial speed (kinetic energy). We could call this situation an *effective* trip. The minimum kinetic energy required is analogous to the *activation energy* for a reaction. If the ball does not have enough kinetic energy, it will not reach the top of the track and will just roll back to point A. This is like two molecules colliding without enough energy to rearrange their bonds—they just rebound elastically.

Note that a ball that returns to point A will have the same kinetic energy it began with, but a ball that makes it to point B will have more kinetic energy (but less potential energy) because it will be moving faster. The example above is also analogous to the enthalpy change for an exothermic reaction. The enthalpy change (net chemical energy change) results in energy being immediately released to neighbouring entities. These entities then move faster, collide with more energy, and are more likely to react. For example, the energy released when the first few molecules of hydrogen and oxygen react (initiated by a spark or flame) is quickly transferred to other molecules, allowing the reaction to proceed unaided by external sources of energy (**Figure 4**). The reaction, once begun, is self-sustaining as long as enough reactants remain to make collisions likely. Exothermic reactions, once begun, often drive themselves.

An Analogy for Activation Energy

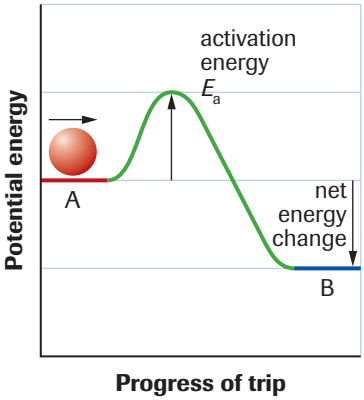


Figure 3
On a trip from A to B, there is a net decrease in potential energy, but there must be an initial increase in potential energy (activation energy) for the trip to be possible.

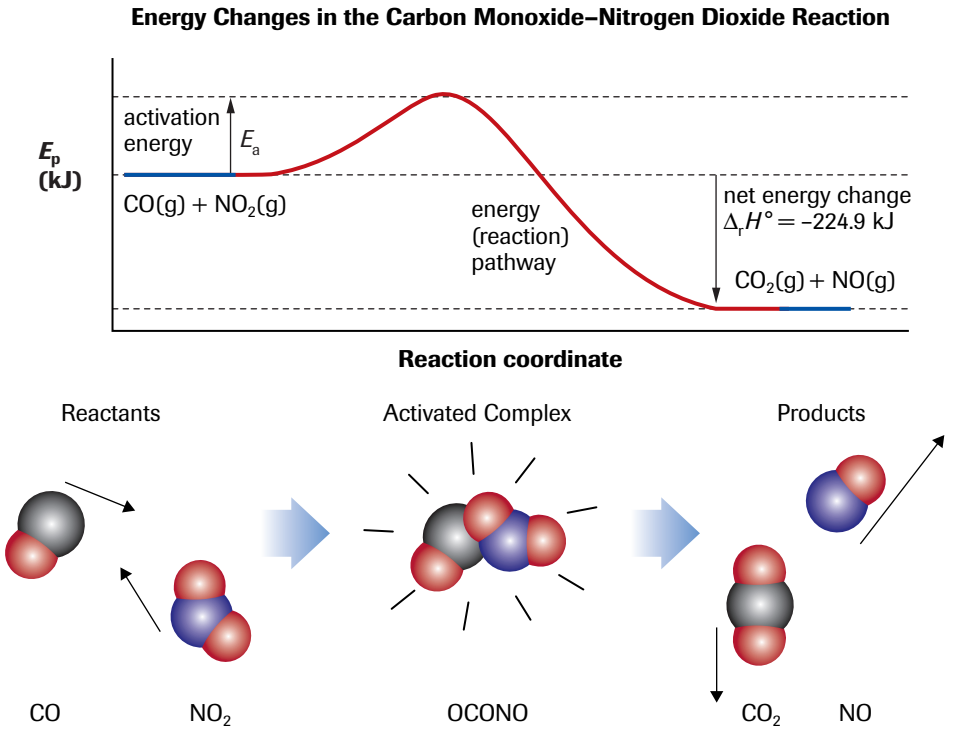
Figure 4
The self-sustaining exothermic reaction of hydrogen and oxygen requires only a single spark to provide the initial energy of activation and start the reaction. This is useful when desired, as in the operation of the space shuttle main engines **(a)**, and disastrous in other cases, as in the explosion of the German airship *Hindenburg* in Lakehurst, New Jersey, in 1937 **(b)**. The exothermic reactions generate a continuous supply of energy to sustain the reaction.

Consider the reaction of carbon monoxide with nitrogen dioxide, plotted as potential energy of the molecules versus progress of reaction; that is, the progress over time of the molecular activity that constitutes the reaction (**Figure 5**, page 528).

$$CO(g) + NO_2(g) \rightarrow CO_2(g) + NO(g) \qquad \Delta_r H° = -224.9\ kJ$$

In Figure 5, the molecular collision follows an energy (or reaction) pathway along the plot from left to right. The *energy pathway* is the relative potential energy of the chemical system as it moves from reactants through activated complex to products. The *activated complex* is the chemical entity containing the collided reactants. Along the flat

Figure 5
The energy pathway and the models represent a theoretical explanation of the reaction. The activation energy explains both the initiating energy required and the rate for this particular reaction.



Learning Tip

To draw these energy pathway diagrams, start with determining, if possible, the absolute or relative initial and final energy. Then add an energy pathway with an estimate of the activation energy between the initial and final values.

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region on the left, the molecules are moving toward each other, but are still distant from each other. As the molecules approach more closely, they are affected by repulsion forces and begin to slow down. Some of their kinetic energy is changed to chemical potential energy, and is stored as a repelling electric field between them. If the molecules have enough kinetic energy—which means more energy than is required to get to the energy level of the activated complex—they can approach closely enough for their bond structure to rearrange. The activated complex occurs at the maximum potential energy point in the change along the energy pathway.

In the carbon monoxide–nitrogen dioxide example, the energy initially absorbed to break the nitrogen–oxygen bond is less than the energy released when a new carbon–oxygen bond forms. Repulsion forces push the product molecules apart, converting potential energy to kinetic energy. If the overall energy change is obtained by comparing reactants and products at the same temperature, the difference is observed as a net release of energy to the surroundings. If the energy change is measured at constant pressure (the usual situation for a reaction open to the atmosphere), it is called the enthalpy change, $\Delta_r H$, which is -224.9 kJ at standard conditions for this particular (exothermic) example (**Figure 6**).

EXTENSION

Reaction Coordinate Diagrams

This simulation will take you a little further in your understanding of communicating energy changes during chemical reactions.

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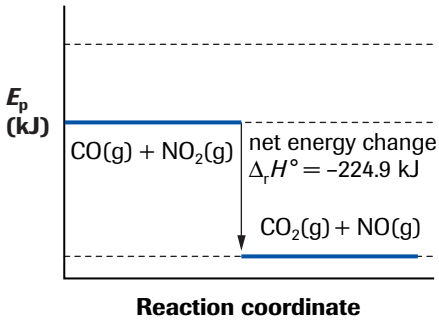

Figure 6
Chemical potential energy diagram for the carbon monoxide–nitrogen dioxide reaction

Chemists infer that, if a large quantity of energy is needed to start a reaction and if the reaction progresses relatively slowly, then the activation energy is large. A spontaneous reaction at room temperature and a higher rate of reaction is interpreted as a relatively small activation energy.

Recall the chemical potential energy diagrams showing enthalpy changes in Chapter 11 and Figure 6. The new energy pathway diagrams (such as Figure 5) show the energy pathway between the initial and the final energy states. You can think of the new energy pathway diagrams as being an expanded form of chemical potential energy diagram, with the approximate energy of the activated complex also represented.

The carbon monoxide–nitrogen dioxide reaction is exothermic: the potential energy of the products is less than that of the reactants. If the reverse were true—if the potential energy of the products were greater than that of the reactants—the reaction would be endothermic. A continuous input of energy, usually heat, would be needed to keep the reaction going, and the enthalpy change would be positive (**Figure 7**).

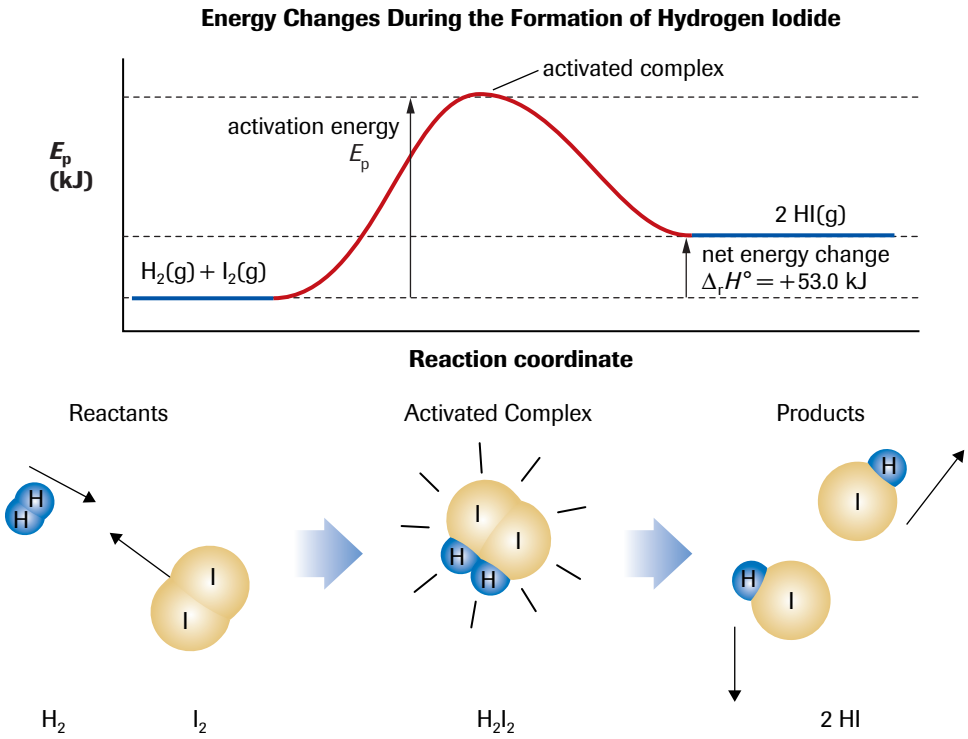

Figure 7
In this example the graph and the models represent the theory that chemists use to explain the "kick-start" that a reaction needs and the continuing rate of reaction afterwards.

Learning Tip

In Chapter 11 you drew mostly chemical potential energy diagrams with E_p on the *y*-axis (with no values). You also saw some enthalpy change diagrams with $\Delta_f H$ and numerical values on the *y*-axis. For energy pathway diagrams, E_p (with no values) is a more appropriate axis label because it is not possible to measure an enthalpy change, under standard conditions, for reactants to activated complex, and from activated complex to products.

WEB Activity

Simulation—Collision–Reaction Theory

View a simulation to review some key points of the collision–reaction theory including activation energy and enthalpy changes.

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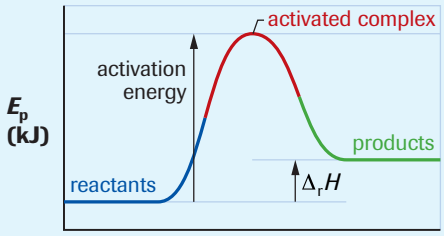
COMMUNICATION example

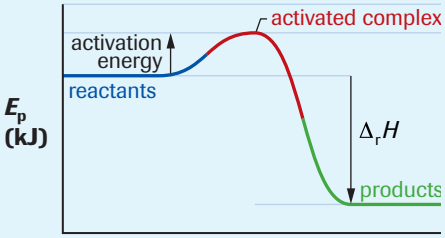
Draw energy pathway diagrams for a general endothermic and a general exothermic reaction. Label the reactants, products, enthalpy change, activation energy, and activated complex.

Solution

Potential Energy Changes During an Endothermic Reaction



Potential Energy Changes During an Exothermic Reaction



Activation Energy and Ozone

Research indicates that the energy of a photon of electromagnetic radiation is inversely proportional to the wavelength. The longer the wavelength, the lower the energy of the radiation. Ozone (O_3) is formed and destroyed naturally in the stratosphere by ultraviolet (UV) radiation from our sun providing the activation energy. Ozone is formed by converting molecular oxygen (O_2) into atomic oxygen (O). The atomic oxygen then reacts with molecular oxygen to produce ozone:

$$O_2(g) + \sim 240 \text{ nm UVC} \rightarrow O(g) + O(g)$$

$$O(g) + O_2(g) \rightarrow O_3(g)$$

The ozone molecule is then split when it absorbs skin-cancer causing UVB radiation.

$$O_3(g) + 240\text{–}320 \text{ nm UVB} \rightarrow O_2(g) + O(g)$$ (which then reacts to replenish the ozone)

The energy supplied by the sun's UV radiation is a measure of the activation energy for these reactions; that is, the activation energy (from UVB) for destroying ozone is lower than the activation energy (from UVC) for converting molecular oxygen to atomic oxygen. In the laboratory chemists can perform controlled experiments with electromagnetic radiation to determine the activation energy for reactions.

DID YOU KNOW ?

Ozone Depletion Hypothesis

Over thirty years of research supports the ozone depletion hypothesis. Parallel chemical research efforts show that the natural concentration of ozone in the stratosphere is being reduced by technology-produced chemicals. For example, air conditioner and fire-fighting CFCs (chlorofluorocarbons) are decomposed by radiation to produce atomic chlorine. This atomic chlorine reacts with ozone to reduce the ozone concentration. Evidence for this reaction is the existence of ClO(g) in the stratosphere.

WWW WEB Activity

Web Quest—Neurotransmitters and Nerve Agents

This Web Quest requires you to actively research how chemistry could be used in a dangerous and deadly way. Work as a team to develop informational posters for emergency response personnel, outlining how nerve agents work and how to treat individuals who have been exposed to nerve agents. You will explain the normal functions of nerves, referring to the action of biological catalysts. You can also research how nerve agents affect nerve impulses to cause symptoms, and outline appropriate treatment.

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Section 12.1 Questions

1. Describe, in your own words, what happens in a successful reaction of two molecules. Include as many key points as possible from the beginning to the end of the reaction.
2. What types of experiments led to the hypothesis that reactions have an activation energy?
3. (a) Is the reaction in **Figure 8** endothermic or exothermic?
   (b) What do (i) and (ii) represent?
   (c) Explain the energy changes that occur at different points during the reaction progress, referring to potential and kinetic energy.

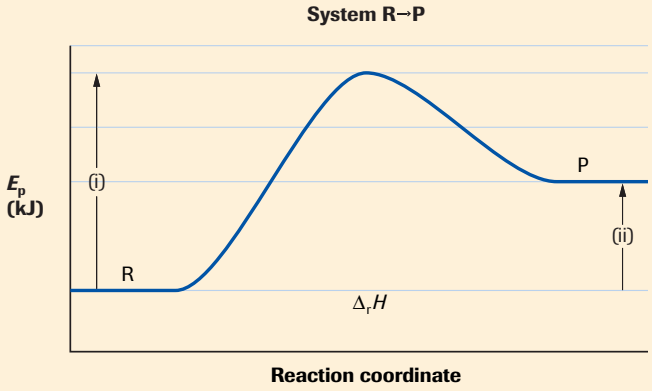

Figure 8
An energy pathway diagram

4. Enthalpy change and activation energy are two important concepts used when describing a chemical reaction. How are these two terms similar, and how are they different?
5. The combustion of hydrogen to produce water is a well-studied chemical reaction. Hydrogen may become one of the most important fuels in the future—for heat, transportation, and electricity. If possible, present your responses to the following questions electronically.
   (a) What theoretical conditions are necessary for this reaction to occur?
   (b) Draw an enthalpy change diagram for the combustion of hydrogen to form liquid water. Include actual enthalpy of formation values. Use whole-number coefficients in the chemical reaction equation.
   (c) Assuming a one-step reaction, draw an energy pathway diagram.
   (d) Label the reactants, products, enthalpy change, activation energy, and activated complex.

Use this information to answer questions 6 and 7.

You may have seen a video or a demonstration of the relative rates of reaction of the alkali metals—sodium, potassium, and cesium—with water (**Figure 9**). This evidence suggests that there is an increasing rate of reaction from sodium through cesium.

Figure 9
Different reactants, like the alkali metals placed in water, have a different rate of reaction. Sodium fizzes while potassium bursts into flames. Cesium is even more reactive.

6. Complete the Purpose, Problem, Hypothesis, Prediction, Design, Materials (including cautions), and Procedure for an investigation to test the hypothesis that the activation energy decreases from sodium to cesium.
7. Draw three energy pathway diagrams with relative activation energies, for the reactions.

Extension

8. Aboriginal peoples used fire for many purposes. What technologies did they use to start a fire?

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9. List the ignition temperature of a few combustible materials that interest you. Write a brief theoretical explanation for the different ignition temperatures.

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10. For thousands of years, peoples living in cold climates have taken advantage of the low temperatures to help them preserve food.
    (a) Apply the concepts learned in this section to create a hypothesis to explain why food lasts longer at low temperatures.
    (b) Research a technology that was developed to capitalize on the benefits of cold storage. Consider the risks and benefits of this technology.
    (c) Create an illustrated article entitled "Cold Storage: Theory and Application" suitable for publication in a popular science magazine or e-zine.

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12.2 Bond Energy and Reactions

Figure 1
In the human body, the metabolism of fats and carbohydrates is an exothermic reaction. Athletes like Jordin Tootoo and Todd Simpson need to "fuel up" before competing.

Figure 2
In some Aboriginal cultures, the visual effects of electricity are seen as energy transfers. In Western science, we describe similar energy transfers. Plants, such as this fiddlehead fern, grow by increasing the complexity and number of electron bonds between atoms in the process of photosynthesis. When we eat food, we break down the chemical bonds and reassemble them, resulting in energy being released, the growth of cells, and the production of heat. Our nerves and brain function all occur because of the transfer of energy by electrons.

Energy transfer is an important factor in all chemical changes. Exothermic reactions, such as the combustion of gasoline in a car engine and the metabolism of fats and carbohydrates in the human body (**Figure 1**), release energy into the surroundings. Endothermic reactions, such as photosynthesis (**Figure 2**) and the decomposition of water into hydrogen and oxygen, remove energy from the surroundings. Knowledge of energy and energy changes is important to society and to industry; the study of energy changes provides chemists with important information about chemical bonds.

Just as glue holds objects together, electrical forces hold atoms together. In order to pull apart objects that are glued together, you have to supply some energy. Similarly, if atoms or ions are bonded together, energy (in the form of heat, light, or electricity) is required to separate them. In other words, bond breaking—when two entities (such as atoms or ions) move apart—requires energy.

bonded particles + energy $\rightarrow$ separated particles

In contrast, bond making—when two entities move together—releases energy.

separated particles $\rightarrow$ bonded particles + energy

By analogy it requires energy to lift an object away from Earth, while energy is released when an object is dropped to Earth.

The stronger the bond holding the particles together, the greater the quantity of energy required to separate them. **Bond energy** is the energy required to break a chemical bond. It is also the energy released when a bond is formed. Even the simplest of chemical reactions involves the breaking and forming of several individual bonds. The terms *endothermic* and *exothermic* are empirical descriptions of overall changes that scientists explain by their knowledge of bond changes.

Some reactions might involve several steps, with several unstable intermediate products along the way. For simplicity, however, we will just consider the energy changes between the initial reactants and the final products.

Endothermic Reactions

Consider the decomposition of water:

$$2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \qquad \Delta_r H° = +571.6\ kJ$$

In this reaction, hydrogen–oxygen bonds in the water molecules must be broken, and the hydrogen–hydrogen and oxygen–oxygen bonds must be formed.

Since the overall change is endothermic, the energy required to break the O—H bonds must be greater than the energy released when the H—H and O═O bonds form. In any endothermic reaction, more energy is needed to break bonds in the reactants than is released by bonds formed in the products.

Exothermic Reactions

For exothermic reactions, the opposite is true. More energy is released by bonds formed in the products than is needed to break bonds in the reactants. The reaction between hydrogen and chlorine (**Figure 3**) illustrates the energy of bond breaking and bond making. Although an activated complex may be involved in the transition from bond breaking to bond making, for simplicity, we will only look at the individual bonds that are changing. Energy is required to break the bonds in hydrogen molecules (H_2) to create hydrogen

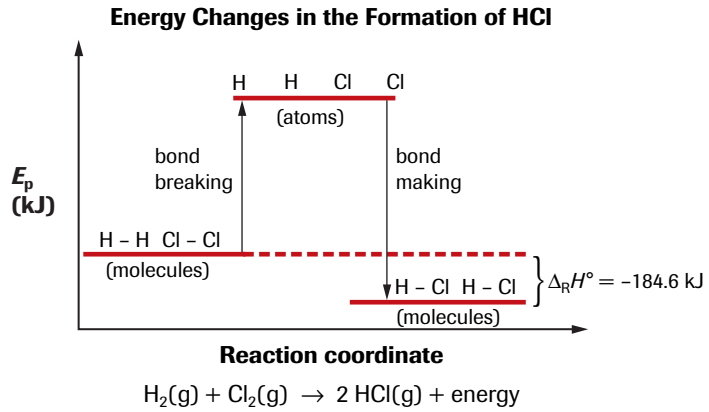

Figure 3
Energy is absorbed in order to break the H–H and Cl–Cl bonds, but more energy is released when the H–Cl bonds form. The overall result is an exothermic reaction.

atoms (H). The two hydrogen atoms have higher chemical potential energy than a hydrogen molecule. Likewise, the chlorine atoms have higher potential energy than the chlorine molecules. When the hydrogen and chlorine atoms make bonds to create hydrogen chloride molecules, energy is released. Since this reaction is exothermic, the logically consistent explanation is that more energy is released by bond making than is required for bond breaking. We can communicate this explanation using a potential energy diagram.

The explanation above assumes that sufficient energy is initially added to equal or exceed the required activation energy. This energy may be provided in a variety of forms: heat, light, or electrical. In all cases, the exothermic nature of this reaction means that heat is transferred to the surrounding molecules, thus increasing their kinetic energy.

Bond energies are the fourth method that you have encountered for predicting or explaining a change in enthalpy for a chemical reaction. Although there are quantitative values for bond energies, and scientists can predict a change in enthalpy from bond energies, this is not part of our study in this course. The methods that you have studied for predicting and/or explaining a change in enthalpy are the following:

1. calorimetry: the change in enthalpy equals the change in thermal energy
2. Hess' law: the change in enthalpy equals the sum of component enthalpy changes
3. molar enthalpies of formation: the change in enthalpy equals the enthalpies of formation of the products minus the enthalpies of formation of the reactants
4. bond energies: the change in enthalpy equals the energy released from bond making minus the energy required for bond breaking

All of these methods are logically consistent with each other: they all support each other, moving from more empirical to more theoretical. Every method also yields the same answer to the question "What is the change in enthalpy for a particular reaction?"

SUMMARY Bond Energy and Enthalpy Changes

- Bond energy is the energy required to break a chemical bond; it is also the energy released when a bond is formed.
- The change in enthalpy represents the net effect from breaking and making bonds.
  $\Delta_r H =$ (energy released from bond making) $-$ (energy required for bond breaking)
  Exothermic reaction: making $>$ breaking ($\Delta_r H$ is negative.)
  Endothermic reaction: breaking $>$ making ($\Delta_r H$ is positive.)

DID YOU KNOW?

Unanswerable Questions

In chemistry we use the concept that energy can neither be created nor destroyed. Biology has a similar concept: that all cells come from preexisting cells. These concepts are not intended to address the ultimate question of where the original energy (or cells) came from. They do, however, give us a starting point for our studies. Western science asks specific questions, often about isolated parts of nature. Other cultures look at these big questions in other ways. Aboriginal cultures, for example, often take a more holistic approach to their investigation of nature and natural processes.

EXTENSION

Bond Length and Bond Energy

Using a specific example of bond length versus bond energy, this audio clip will enrich your understanding of bond energy as it relates to bond length and multiple bonds.

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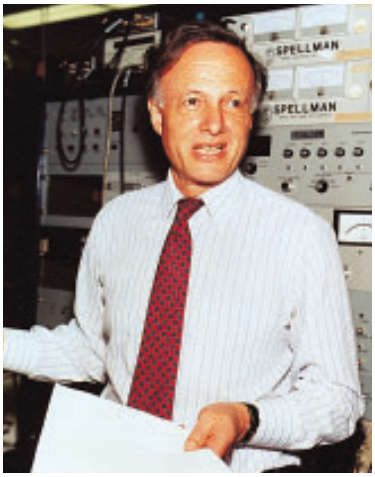

Figure 4
John Polanyi (1929–) of the University of Toronto is a Nobel laureate in chemistry.

WEB Activity

Canadian Achievers—John Polanyi

Dr. John C. Polanyi (**Figure 4**), Canadian Nobel laureate, has refined the empirical and theoretical descriptions of molecular motions during chemical reactions and has published many scientific papers on this subject, known as *reaction dynamics*. He predicted the conditions required for the operation of a chemical laser, and saw his prediction verified by subsequent experiments.

> *"Those of us who are scientists, and those of us who are not, should rid ourselves of the absurd notion that science stands apart from culture. Today, science permeates our lives—our doing and our thinking."*
>
> *John Polanyi*

1. A laser is a technology that allowed new science to be done. Find some examples of chemistry that were allowed due to the invention of the laser.
2. If a laser is chosen by a chemist to initiate and/or maintain a chemical reaction, what does this say about the activation energy of the reaction?
3. What else is Polanyi well known for, besides his chemistry research?

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Section 12.2 Questions

1. Write two definitions of bond energy.
2. Explain how bond energies are related to the activation energy for a reaction.
3. Why must chemical reactions include both the breaking of bonds and the forming of bonds?
4. Draw a chemical potential energy diagram (similar to Figure 3 on page 533) for the decomposition of liquid water into hydrogen and oxygen gases. Illustrate the energy change for the breaking of water molecules into atoms and then for the subsequent formation of hydrogen and oxygen molecules.
5. (a) Explain why the decomposition of water is an endothermic process.
   (b) Explain why the burning of hydrogen is an exothermic process.
6. Predict whether the reaction of hydrogen with bromine is endothermic or exothermic. Making reference to bond energies, explain your prediction.
7. In the Exploration activity (page 523) you looked at the reactions of metals with hydrochloric acid, and in Investigation 11.3 (pages 507 and 517) you determined the enthalpy change for the reaction of magnesium with hydrochloric acid.
   (a) Draw a chemical potential energy diagram, including the enthalpy change, for the reaction of magnesium metal with hydrochloric acid.
   (b) Using the net ionic equation for this reaction, list the bonds that must be broken in the reactants and the bonds that must be formed in the products.
   (c) Suggest a possible theoretical hypothesis to explain the empirical differences in the rates of reaction of zinc, magnesium, and iron with hydrochloric acid. Identify any assumptions you are making.
8. The reaction of hydrogen with chlorine at room temperature, in the absence of light, is undetectable owing to the very slow rate of reaction. The same reaction is explosively fast, however, if exposed to sunlight. The following mechanism has been suggested for this reaction.

$$Cl_2(g) + \text{light energy} \rightarrow Cl(g) + Cl(g)$$
$$Cl(g) + H_2(g) \rightarrow HCl(g) + H(g)$$
$$H(g) + Cl_2(g) \rightarrow HCl(g) + Cl(g)$$
$$Cl(g) + Cl(g) \rightarrow Cl_2(g)$$

   (a) Write the net overall reaction equation.
   (b) Identify the intermediate entities that are formed during the step-by-step reaction process.
   (c) Discuss the activation energy for the collision of molecular chlorine with molecular hydrogen, and for the collision of atomic chlorine with molecular hydrogen. Which reaction has the greater activation energy, and what evidence can you use to support your argument?
9. The reaction of hydrogen and oxygen (see Figure 4, page 527) is exothermic and self-sustaining. Write the equation for this reaction, and provide a reason why it is not likely that the reaction occurs as a single step.

Extension

10. Ozone formation and destruction are natural bond-making and bond-breaking processes in the stratosphere. (See page 530.)
    (a) What is the source of the energy for breaking bonds?
    (b) Why is shorter wavelength radiation required to break the oxygen bond(s) than to break the ozone bond(s)?
    (c) If energy is produced by making ozone from molecular and atomic oxygen, why can't this energy be used to break more molecular oxygen into atomic oxygen in the stratosphere?

Catalysis and Reaction Rates 12.3

Empirical Effect of Catalysis

Catalysis deals with the properties and development of catalysts, and the effects of catalysts on the rates of reaction. A **catalyst** is a substance that increases the rate of a chemical reaction without being consumed itself in the overall process. The chemical composition and amount of a catalyst are identical at the start and at the end of a reaction. A catalyst reduces the quantity of energy required to start the reaction, and results in a catalyzed reaction producing a greater yield in the same period of time (even at a lower temperature) than an uncatalyzed reaction. Research indicates that the use of a catalyst does not alter the net enthalpy change for a chemical reaction. In green plants, for example, the process of photosynthesis can take place only in the presence of the catalyst chlorophyll (**Figure 1**). Most catalysts significantly accelerate reactions, even when present in very tiny amounts compared with the amount of reactants present.

The action of catalysts seriously perplexed early chemists, who had problems with the concept of something obviously being involved in a chemical reaction but not being changed by that reaction. Effective catalysts for reactions have almost all been discovered by purely empirical methods—trying everything to see what worked.

Chemists learned early that metals prepared with a large surface area (powder or shavings) catalyze many reactions, including the decomposition of hydrogen peroxide in the presence of a platinum catalyst. Many people who wear contact lenses know about this reaction. They use it daily to clean their lenses.

A common consumer example of catalysis today is the use of platinum, palladium, and rhodium in catalytic converters in car exhaust systems (**Figure 2**). These catalysts speed the combustion of the exhaust gases so that a higher proportion of the exhaust will be the relatively harmless, completely oxidized products. Catalysts are extremely important in chemical technology and industry because they allow the use of lower temperatures. This not only reduces energy consumption but also prevents the decomposition of reactants and products and decreases unwanted side reactions. The result is an increase in the efficiency and economic benefits of many industrial reactions. For many industrial processes the difference between success and failure depends on the use of catalysts because they make the reactions fast enough to be profitable. (For an example of this, see The Haber Process case study, in Chapter 8.)

Compounds that act as catalysts in living systems are called enzymes. **Enzymes** are usually extremely complex molecules (proteins). A great many physiological reactions, such as metabolism, are actually controlled by the amount of enzyme present. Enzymes are also of great importance for catalyzing reactions in the food, beverage, cleaner, and pharmaceutical industries.

Figure 1
Green plants contain chlorophyll, which acts as a catalyst in a reaction that splits water molecules into oxygen and hydrogen ions. This reaction is the first step in the process of photosynthesis, which converts carbon dioxide and water into glucose and oxygen.

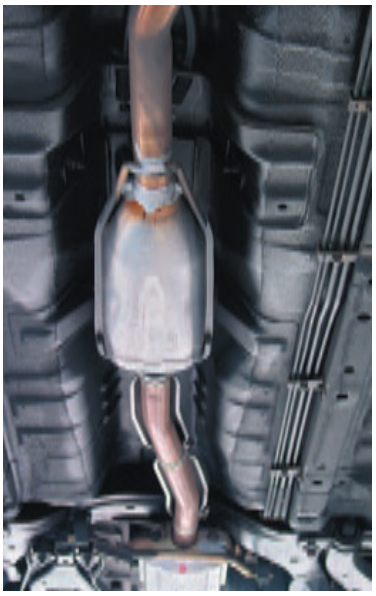

Figure 2
Many commercial and industrial catalysts are heterogeneous, which means that they provide a solid surface upon which the reactants can be absorbed and reacted. The catalytic converter in a car is a good example of a heterogeneous catalyst. The inner surface of the catalytic converter is coated with an alloy containing platinum, rhodium, and palladium.

Practice

1. Do technologists normally use empirical or theoretical knowledge when doing work that involves catalysts?
2. List some technological inventions that involved the use of catalysts.
3. List some natural (biological) processes that involve the use of catalysts.
4. Enzymes in your body are generally present in extremely small quantities, but any substances that affect your enzymes are almost always very toxic and dangerous. Explain why this should be so, referring to reaction rates in your explanation.

INVESTIGATION 12.1 *Introduction*

Iodine Clock Reaction

Technological problem solving often involves a systematic trial-and-error approach that is guided by knowledge and experience. Thomas Edison, the greatest inventor of all time, used this method, for example, to invent the incandescent light bulb and when making batteries. Usually, one variable at a time is manipulated. In this investigation, a variety of potential catalysts are added one at a time to a reaction mixture. The rate of the reaction, as determined by the time required to get to a blue endpoint, is the responding variable.

Use MSDS to find cautions. Include safety and disposal information at the end of the Materials section.

Report Checklist

- ○ Purpose
- ○ Problem
- ○ Hypothesis
- ○ Prediction
- ● Design
- ● Materials
- ● Procedure
- ● Evidence
- ● Analysis
- ● Evaluation (1, 3)

Purpose

The purpose of this investigation is to create a generalization about the relative effect that potential catalysts have on the rate of a chemical reaction.

Problem

What is the relative effect of the chemicals tested as potential catalysts for increasing the rate of the iodine clock reaction?

To perform this investigation, turn to page 543.

DID YOU KNOW

Bread Making

Bread making is an example of chemical kinetics. Yeast (one-celled fungi) is added to produce enzymes, which catalyze several reactions to produce, for example, carbon dioxide. Gases cause the bread to rise and be less dense.

Figure 3
Bread machines are designed to allow the reactions to take place at the optimum temperatures, which change throughout the process.

DID YOU KNOW

Inhibitors

Some substances are known to slow or stop reactions. Chemists and biochemists believe that these inhibitor substances act differently from catalysts, controlling the reaction rate in a completely different way. Preservatives are inhibitors added to foodstuffs to delay deterioration.

Theoretical Explanation of Catalysis

Chemists believe that catalysts accelerate a reaction by providing an alternative lower-energy pathway from reactants to products. That is, a catalyst allows the reaction to occur by a different activated complex, but resulting in the same products overall. If the new pathway has a lower activation energy, a greater fraction of molecules possess the minimum required energy and the reaction rate increases. Since the activation energy is lowered by exactly the same amount for the reverse reaction, the rate of any reverse reaction increases as well (**Figure 4**).

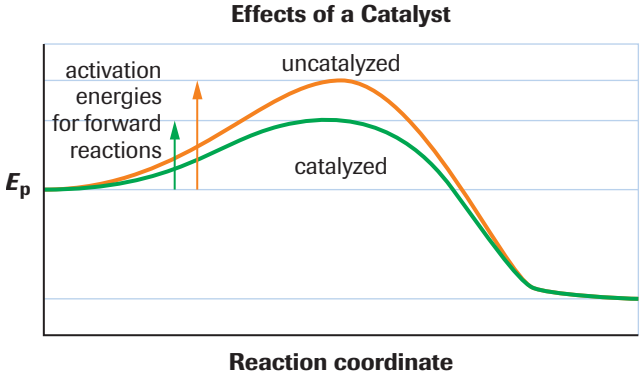

Figure 4
The catalyzed pathway has a lower activation energy, so more collisions lead to a successful reaction.

Scientists do not really understand the actual mechanism by which catalysis occurs for most reactions, and discovering effective catalysts has traditionally been an empirical process involving trial-and-error. Chemists have studied a few catalyzed reactions in detail, so they believe they understand the changes involved. Most of the catalysts (enzymes) for biological reactions work by shape and orientation. They fit substrate proteins into locations on the enzyme as a key fits into a lock, enabling only specific molecules to link or detach on the enzyme, as shown in **Figure 5**.

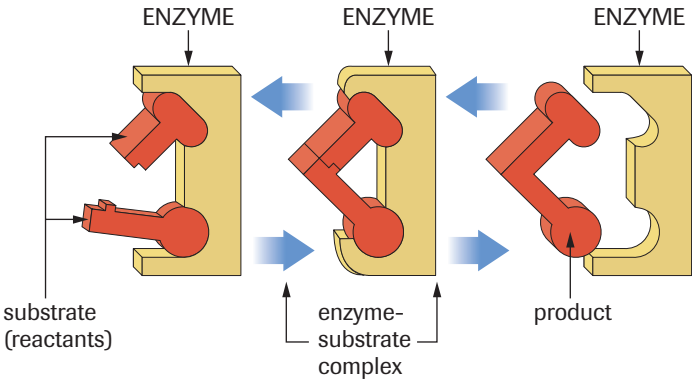

Figure 5
Note that the enzyme shape is specific for the reactant (substrate) molecules. Almost all enzymes catalyze only one specific reaction.

One well-understood non-biological reaction is the decomposition of methanoic (formic) acid in aqueous solution. At room temperature this reaction is very slow, with no noticeable activity (**Figure 6**). When strong acid is added, the solution begins to bubble. Testing indicates that carbon monoxide gas is being produced. If this reaction proceeds until all the formic acid has been consumed, the solution will still contain the same quantity of acid as was initially added. It does not seem to matter which strong acid is added, so we assume that the acting catalyst is the aqueous hydrogen ion, which is common to all aqueous acidic solutions. **Figure 8** shows the energy pathway diagram of the reaction with a catalyst. Note that, like all catalysts, the H^+ is regenerated and, therefore, is not consumed during the reaction. In a catalyzed reaction, catalysts react with one or more of the reactants, but then are regenerated by the end of the reaction.

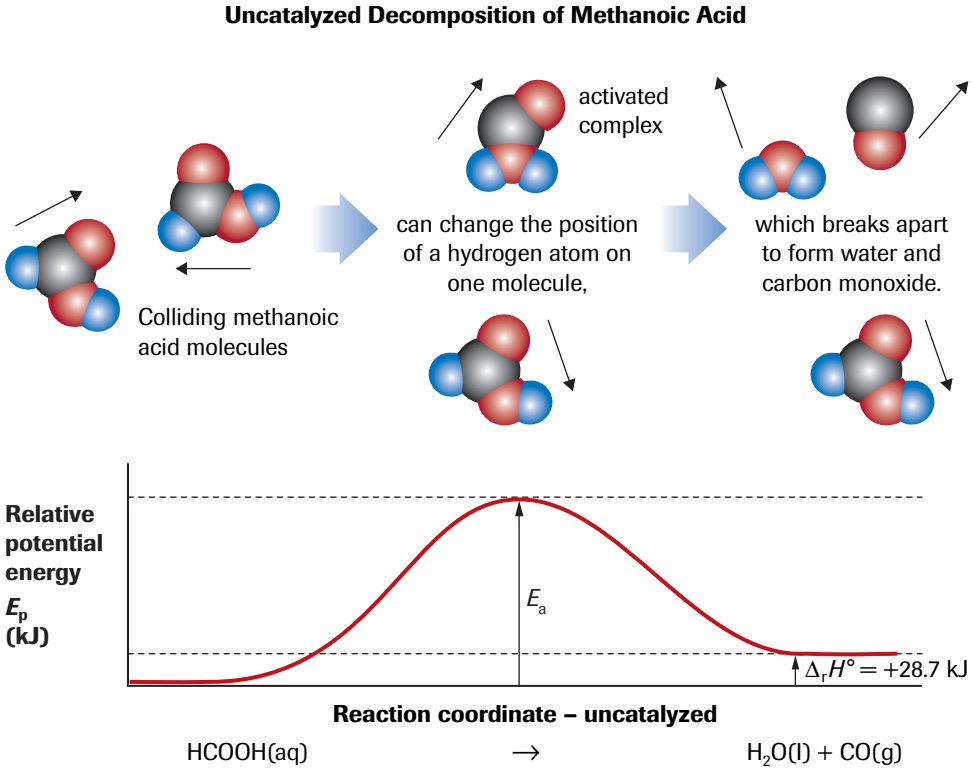

Figure 6
The uncatalyzed reaction proceeds too slowly to notice at room temperature. Note that this reaction is endothermic, requiring an overall increase in (input of) energy.

DID YOU KNOW ?

Hot Beetle Juice

The bombardier beetle of South America has a unique way of protecting itself. When it is threatened, it pumps stored hydroquinone and hydrogen peroxide from one chamber in its body into another chamber. In the second chamber the enzymes catalase and peroxidase mix with the stored compounds. The resulting catalyzed exothermic reaction produces a hot, corrosive liquid that is sprayed at the attacker.

Figure 7
The beetle's spray can cause a skin burn that lasts for several days.

EXTENSION

CBC radioONE
QUIRKS & QUARKS

Bombardier Beetles

A British professor of thermodynamics is researching the bombardier beetle's squirting ability, with the aim of developing a device that will relight extinguished jet engines.

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EXTENSION

Catalysts and Reaction Mechanisms

With more details on the steps during catalysis, this audio clip will enrich your understanding of how catalysts can alter a reaction mechanism and hence speed up a reaction.

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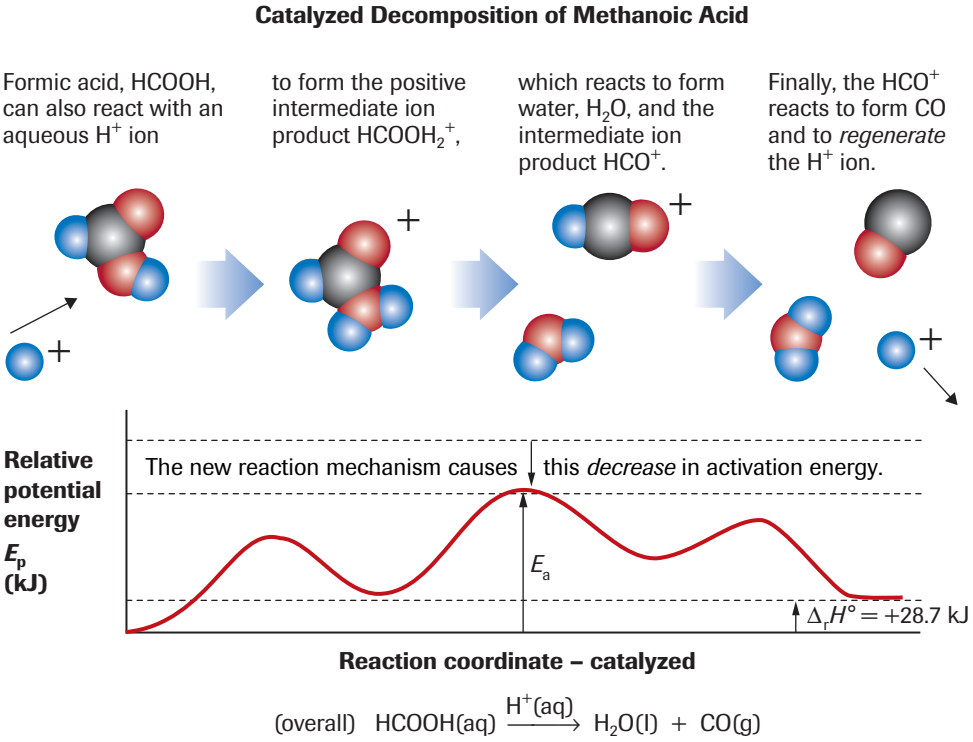
Catalyzed Decomposition of Methanoic Acid
Formic acid, HCOOH, can also react with an aqueous H^+ ion
to form the positive intermediate ion product $HCOOH_2^+$,
which reacts to form water, H_2O, and the intermediate ion product HCO^+.
Finally, the HCO^+ reacts to form CO and to *regenerate* the H^+ ion.
Relative potential energy E_p (kJ)
The new reaction mechanism causes this *decrease* in activation energy.
E_a
$\Delta_r H° = +28.7$ kJ
Reaction coordinate – catalyzed
(overall) $HCOOH(aq) \xrightarrow{H^+(aq)} H_2O(l) + CO(g)$

Figure 8
The catalyzed reaction proceeds rapidly enough to produce bubbles of carbon monoxide gas at room temperature. A higher fraction of the molecular collisions become effective because the activation energy is lower. Catalysts are normally written above the reaction arrow in a reaction equation.

DID YOU KNOW?

Communication Through Journals

The German chemist Justus von Liebig wrote in 1834: "Chemical literature is not to be found in books, it is contained in journals." Refereed journals are regularly published reports of research that have passed a panel of judges. (See Appendix B.4.) For example, Johann Döbereiner discovered in 1823 that platinum catalyzes the burning of hydrogen. Within three months this discovery was reported in about a dozen European science journals.

DID YOU KNOW?

Chemical Marriage

The Chinese symbol for *catalyst* is the same as that used for *marriage broker*.

觸媒

Catalysis and the Nature of Science

The practice of science uses two important kinds of reasoning—inductive and deductive. *Inductive reasoning* involves extending specific examples to obtain a general statement; for example, using the evidence from an experiment to form a hypothesis in the analysis section of an investigation report. *Deductive reasoning* involves applying a general concept such as a theory, law, or generalization to obtain (deduce) a specific instance.

Chemists use indirect and direct evidence to hypothesize the reaction pathway for uncatalyzed and catalyzed reactions. They create hypotheses for the structures of the activated complexes, and hypotheses for the individual reaction steps in an overall reaction. A *reaction mechanism* describes the individual reaction steps and the intermediates formed during the reaction, starting with reactants and finishing with products. **Intermediates** are chemical entities that form with varying stability at the end of a step in a reaction mechanism. They are more stable (have lower potential energy) than the activated complexes, but less stable than the reactants and the products. The intermediate then reacts in a subsequent step and does not appear in the final reaction mixture. For example, a three-step reaction mechanism (Figure 8) can be generalized as follows:

Step 1: reactant(s) $\rightarrow$ activated complex 1 $\rightarrow$ intermediate 1
Step 2: intermediate 1 $\rightarrow$ activated complex 2 $\rightarrow$ intermediate 2
Step 3: intermediate 2 $\rightarrow$ activated complex 3 $\rightarrow$ product(s)

The inductive reasoning of using the evidence from an experiment to hypothesize a reaction mechanism is usually accompanied by deductive reasoning to test the logic of

the mechanism. Chemists constantly ask themselves if a hypothesis makes sense based upon all the evidence they have collected and all of their chemical experience. If the mechanism has internal consistency, all the intermediates and reaction steps seem to be correct/logical. If the mechanism has external consistency, none of the thinking behind the proposed mechanism contradicts accepted theories, laws, or generalizations.

For example, evidence from sophisticated technologies (such as spectrometers) suggests that there are two intermediates in the catalyzed decomposition of methanoic acid. The spectrographs indicate that the chemical formulas of the intermediates are $HCOOH_2^+(aq)$ and $HCO^+(aq)$. The same equipment provides evidence that the products are water and carbon monoxide. Other diagnostic tests on the final products provide supporting evidence.

A consistency check of the mechanism indicates that all chemical equations must be balanced and that all reactants, intermediates, and products can be accounted for by writing balanced chemical equations. Furthermore, the chemical formulas of all chemicals described are consistent with chemical formulas of known chemicals and/or with the bonding capacity of each atom in each entity. From an energy perspective, the law of conservation of energy seems to be obeyed, the chemical potential energies of the entities involved are consistent with known values, and the enthalpy change remains the same as for the uncatalyzed reaction. It all fits together in a nice logical package. There are no contradictions, no inconsistencies.

Uses of Catalysts

The Oil Industry

The oil industry uses catalysts in the cracking and reforming of crude oil and bitumen to produce more marketable fractions (such as gasoline). The science and engineering of crude oil refining has advanced tremendously, due mostly to the use of catalysts that increase the rate of the reaction while decreasing the energy (which often means decreasing the temperature) required for the chemical process. **Table 1** lists the typical catalysts for cracking and reforming of crude oil.

Table 1 Catalysts Used in the Oil Industry

	Process	Description	Typical catalysts
cracking	fluid catalytic cracking (high temperature)	heavy gas oil to diesel oils and gasoline	zeolite (silicates)
	hydrocracking (lower temperature, higher pressure, presence of H_2)	heavy oil to gasoline and kerosene	Pt(s), Pt(s)/Re(s)
reforming	alkylation	smaller to larger molecules plus increased branching	$H_2SO_4(aq)$, HF(aq)
	catalytic reforming	naphtha to high octane hydrocarbons	Pt(s), Pd(s)

WEB Activity

Simulation—A Catalyzed Reaction

Hydrogenation is an important industrial process. Scientific studies of hydrogenation typically start with simple reactions in order to understand the molecular process (mechanism). In this animation, you will investigate the hydrogenation of ethene using a platinum catalyst.

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DID YOU KNOW

Syrup Digesters

High-fructose corn syrup is a key ingredient in many processed foods: pop, fruit-flavoured drinks, cookies, jam, candy … It is made by treating starch (extracted from corn) with enzymes to break it down into glucose monomers. Glucose, however, is not as sweet as the sucrose (table sugar) that has traditionally been used to sweeten foods. Fortunately, there are enzymes that convert some of the syrup's glucose into super-sweet fructose. It is this combination of glucose and fructose that is so widely used as corn syrup. The mixture can even be tailored to the needs of the food and beverage industries. While 42% fructose syrup is perfectly satisfactory for many foods, a sweeter syrup is required by the soft drink industry: up to 55% fructose.

Learning Tip

You are not expected to memorize which catalyst goes with which chemical process. However, you should know that major reactions, for example, cracking, reforming, and hydrodesulfurization, use catalysts. In fact, the message is that most major chemical processes in industry involve catalysis.

DID YOU KNOW

Gasoline Production

Gasoline is the most marketable of all products from crude oil. In the 1920s about one-quarter of a barrel of oil could be converted to gasoline. Due to the use of modern catalysts, about half of a barrel of oil can now be converted to gasoline.

DID YOU KNOW ?

Greenhouse Gases and Global Warming Potentials

The major greenhouse gases, with their contribution to global warming, are as follows:

$H_2O(g)$ . . . 36%–70%
$CO_2(g)$ . . . 9%–26%
$CH_4(g)$ . . . 4%–9%
$O_3(g)$ 3%–7%

Note that the mixing of these gases provides a range of contribution. The higher end of the range is for the gas alone.

Although accumulated carbon dioxide contributes most to global warming, its global warming potential (GWP) per unit mass is low. The relative GWPs for some chemicals (over a period of one hundred years) are as follows:

GWP	Chemical
1	$CO_2(g)$
21	$CH_4(g)$
310	$N_2O(g)$
12 000	$CHF_3(g)$
22 200	$SF_6(g)$

CAREER CONNECTION

Field Production Operator

The primary responsibility for field production operators is to remove impurities from the oil, gas, or both before transporting to refineries and markets. They may also ensure that the wells and flowlines are maintained and efficient, and that safety regulations are enforced.

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Upgrading of Bitumen from Oil Sands

Oil sand is about 84% bitumen, over 90% of which is recovered from the sand. Over 93% of the Alberta oil sands are located too deep for surface mining and must be recovered *in situ*, that is, the bitumen is recovered from the oil sand without removing the sand. Regardless of whether the oil sands are surface mined or mined *in situ*, the composition of the bitumen is about the same. Bitumen is composed of about 80% aromatic hydrocarbons, which have an average H/C ratio of less than 1. Upgraded bitumen (synthetic crude) contains mostly alkanes and small aromatics with an average H/C ratio of about 2. The ratio is increased during bitumen upgrading by coking (removing carbon) and/or hydrocracking (adding hydrogen). Hydrotreating is used to remove sulfur and nitrogen contaminants and to convert alkynes and alkenes into alkanes. Catalysts play a significant role in two of these chemical processes (**Table 2**).

Table 2 Catalysts Used during Bitumen Upgrading

Stage	Process	Description	Typical catalyst
1a. hydrocracking	cracking and hydrogenation	creates smaller molecules; increases the H/C ratio	(Ni-Mo) sulfide(s) on alumina ($Al_2O_3(s)$)
1b. and/or coking	remove carbon	creates smaller molecules; increases the H/C ratio	no catalyst
2. hydrotreating	hydrogenation to remove S and N	$\ldots S + H_2(g) \rightarrow H_2S(g) + \ldots$ $\ldots N + H_2(g) \rightarrow NH_3(g) + \ldots$	(Ni-Mo) sulfide(s) on alumina ($Al_2O_3(s)$)

Emissions Control

Emissions control is another use of catalysts. These emissions may be nitrogen oxides (from power plants), sulfur (from gas plants), and chemicals that contribute to smog (from internal combustion engines). **Table 3** shows some of the emission control reactions and their catalysts. (You do not need to memorize these reactions and catalysts.)

Table 3 Catalysts Used for Emissions Control

Process	Description	Typical catalysts
NO_x removal from exhaust streams of industrial heat and power generators	NO_x is selectively reduced by reacting with a reagent such as ammonia or urea; e.g., $NO(g)$ and $NO_2(g)$ to $N_2(g)$	V(s), Ti(s), silica, and/or zeolite
sulfur removal using hydrodesulfurization (HDS)	sulfur compounds + $H_2(g) \rightarrow H_2S(g)$ $H_2S(g) \rightarrow S_8(s)$ using Claus process	$MoS_2(s)$/Co(s) alumina
automobile catalytic converter (3-way)[1]	reduction catalyst: $2\,NO(g) \rightarrow N_2(g) + O_2(g)$ $2\,NO_2(g) \rightarrow N_2(g) + 2\,O_2(g)$ oxidation catalyst: $2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g)$ $C_xH_y(g) + n\,O_2(g) \rightarrow x\,CO_2(g) + m\,H_2O(g)$	Pt(s)/Rh(s) Pt(s)/Pd(s)

[1] Modern catalytic converters are called 3-way converters because they use catalysts to convert three pollutants–NO_x, CO, and hydrocarbons–into less harmful substances.

As you can see from the above reactions, catalysis is an extremely important branch of chemistry and chemical engineering. Catalysts play a very important role in chemical industries—for producing chemicals that we use in our work and in our homes and for controlling environmentally harmful emissions.

Enzymes

Natural product chemists have discovered many naturally occurring catalysts. Most of these catalysts are enzymes that increase the rate of specific reactions (**Table 4**).

Chemists are now using enzymes as catalysts for the production of chemicals not found in nature, such as pharmaceuticals and agricultural chemicals. These enzymes are designed to be highly selective in the reaction each catalyzes, effective under ambient conditions, and convenient and safe to dispose.

Table 4 Natural Enzymes as Catalysts

Technological process	Description	Catalyst(s)
detergents with enzymes (widest application of enzymes today) (**Figure 9**)	hydrolyzes (breaks down) starch	amylases
	attacks cellulose fibres to remove tiny fibres and prevent pilling	cellulases
	breaks down oily and fatty stains	lipases
	degrades proteins	proteases
brewing (fermentation)	$C_6H_{12}O_6(s) \rightarrow 2\,C_2H_5OH(l) + 2\,CO_2(g)$	zymase (yeast)
cleaning contact lenses	decomposes $H_2O_2(aq)$ to $O_2(g)$, to disinfect contact lenses	catalase
high-fructose corn syrup	three enzymatic steps: liquefies corn syrup, hydrolyzes sugar, isomerizes glucose	amylase glucoamylase glucose isomerase
Natural process	**Description**	**Catalyst**
nitrogen fixation	converts nitrogen into nitrogen compounds	nitrogenase
photosynthesis	$6\,CO_2(g) + 6\,H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6\,O_2(g)$	chlorophyll

Figure 9
Many laundry detergents contain enzymes to enhance their effectiveness.

INVESTIGATION 12.2 *Introduction*

Evidence for an Activated Complex

Evidence for an activated complex is difficult to obtain. According to reaction theory, catalyzed and uncatalyzed reactions have different activated complexes. Most activated complexes are colourless and fairly unstable. A few, however, are coloured and exist long enough to be observed.

Purpose

The purpose of this investigation is to test the theoretical concept that a catalyzed reaction involves an activated complex different from that in an uncatalyzed reaction.

To perform this investigation, turn to page 543.

Report Checklist

- ○ Purpose
- ○ Problem
- ● Hypothesis
- ○ Prediction
- ○ Design
- ○ Materials
- ○ Procedure
- ● Evidence
- ● Analysis
- ● Evaluation (1, 2, 3)

Problem

What evidence is there for the existence of a different activated complex for a catalyzed reaction when compared to an uncatalyzed reaction?

Design

An uncatalyzed reaction is observed, and then a catalyst is added to the chemical system. Evidence for the formation of a different activated complex is sought.

SUMMARY *Catalysis*

- A catalyst is a substance that increases the rate of a reaction without being consumed in the overall process.
- According to theory, catalysts accelerate a reaction by providing an alternative pathway with a lower activation energy.
- A catalyst does not alter the net enthalpy change of a reaction. Both catalyzed and uncatalyzed versions of the same reaction have the same $\Delta_r H$.
- Catalysts are widely used in industry, consumer technologies, and biological processes.

Section 12.3 Questions

1. Compare two reactions with the same reactants. One reaction involves a catalyst; the other does not.
   (a) What is *the same* for both reactions?
   (b) What is *different* for both reactions?
2. Consider the following reaction mechanism, in which A, B, and E may be elements or compounds, and C, D, and F are compounds:
   (1) $2A + B \rightarrow C$
   (2) $C \rightarrow D$
   (3) $D + E \rightarrow F$
   (a) Which entities are intermediates?
   (b) Which entities are reactants?
   (c) Which entities are products?
   (d) What is the net reaction equation?

Use this information to answer questions 3 to 5.

Consider the energy pathway diagram for the hypothetical reaction in **Figure 10**. This reaction is reversible because, under certain conditions, products will re-form the reactants.

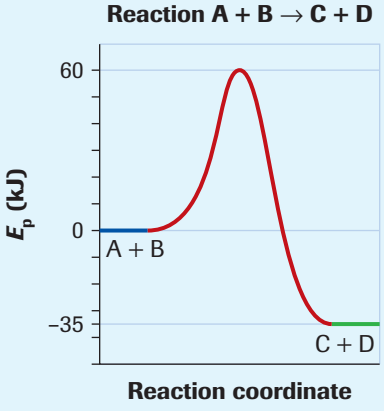

Figure 10
Energy pathway diagram for questions 3 to 5.

3. (a) What is the activation energy for the following net forward reaction?
   $A + B \rightarrow C + D$
   (b) What is the activation energy for the following net reverse reaction?
   $C + D \rightarrow A + B$
   (c) What is the change in enthalpy (net energy change) for the net forward reaction?
   (d) What is the change in enthalpy (net energy change) for the net reverse reaction?
   (e) Which reaction (forward or reverse) is exothermic?
4. Explain what you would expect to occur if the original collision of particles in the forward reaction has a total available kinetic energy equivalent to 55 kJ.
5. Explain what you would expect to occur if the original collision of particles in the reverse reaction has a total available kinetic energy equivalent to 55 kJ.

6. How do catalysts provide solutions to technological problems? Give at least four examples.
7. Complete the Purpose, Design, Materials, Analysis, and Evaluation (2, 3) sections of the following lab report.

Problem
What is the molar enthalpy of decomposition of 20 mL of 2 mol/L aqueous hydrogen peroxide without and with an iron(III) catalyst being added?

Hypothesis
The molar enthalpy of reaction does not change when a catalyst is added.

Evidence
Trial 1:
volume of aqueous hydrogen peroxide = 20.0 mL
volume of 0.1 mol/L sodium hydroxide = 5.0 mL
volume of aqueous iron(III) nitrate = 0 mL
initial temperature of hydrogen peroxide = 21.4 °C
final temperature of hydrogen peroxide = 23.4 °C
time = 10 min
Trial 2:
volume of aqueous hydrogen peroxide = 20.0 mL
volume of 0.1 mol/L sodium hydroxide = 5.0 mL
volume of aqueous iron(III) nitrate = 0.3 mL
initial temperature of hydrogen peroxide = 21.4 °C
final temperature of hydrogen peroxide = 23.4 °C
time = 2 min

Extension

8. Find at least two examples of enzymes and industrial catalysts. Summarize your research to these questions.
   (a) For each of the enzymes or catalysts, record
   - the reaction that is catalyzed
   - how the catalyst was discovered
   - where and how the catalyst or enzyme acts
   - for an enzyme, physiological implications of its presence or deficiency, whether such a condition exists, and, if so, how it is currently treated
   - economic implications of the industrial catalysts' use

   (b) Which of the industrial catalysts has the greatest effect on your own life? Explain.

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9. Catalysts make it possible for us to modify the components of crude oil to meet our many needs and wants. Despite growing research and development into alternative sources of energy, we rely on crude oil for energy more and more each year. What are the risks and benefits of relying on fossil fuels as energy sources?
10. An ad claims wonderful health benefits from a new form of water created with a catalyst. What kinds of authorities would you accept for this claim?

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INVESTIGATION 12.1

Iodine Clock Reaction

Technological problem solving often involves a systematic trial-and-error approach that is guided by knowledge and experience. Thomas Edison, the greatest inventor of all time, used this method, for example, to invent the incandescent light bulb and for inventing new batteries. Usually, one variable at a time is manipulated. In this investigation, a variety of potential catalysts are added one at a time to a reaction mixture. The rate of the reaction, as determined by the time required to get to a blue endpoint, is the responding variable.

Use MSDS to find cautions. Include safety and disposal information at the end of the Materials section.

Report Checklist

○ Purpose	● Design	● Analysis
○ Problem	● Materials	● Evaluation (1, 3)
○ Hypothesis	● Procedure	
○ Prediction	● Evidence	

Purpose

The purpose of this investigation is to create a generalization about the relative effect that potential catalysts have on the rate of a chemical reaction.

Problem

What is the relative effect of the chemicals tested as potential catalysts for increasing the rate of the iodine clock reaction?

INVESTIGATION 12.2

Evidence for an Activated Complex

Evidence for an activated complex is difficult to obtain. According to reaction theory, catalyzed and uncatalyzed reactions have different activated complexes. Most activated complexes are colourless and fairly unstable. A few, however, are coloured and exist long enough to be observed.

Purpose

The purpose of this investigation is to test the theoretical concept that a catalyzed reaction involves an activated complex that is different from that in an uncatalyzed reaction.

Problem

What evidence is there for the existence of a different activated complex for a catalyzed reaction when compared to an uncatalyzed reaction?

Prediction

According to the theory of catalysis, a catalyst increases the rate of a reaction by creating an alternative activated complex with a lower activation energy. The evidence should show that the catalyzed reaction had a different activated complex than did the uncatalyzed reaction.

Design

An uncatalyzed reaction is observed, and then a catalyst is added to the chemical system. Evidence for the formation of a different activated complex is sought.

Report Checklist

○ Purpose	○ Design	● Analysis
○ Problem	○ Materials	● Evaluation (1, 2, 3)
● Hypothesis	○ Procedure	
○ Prediction	● Evidence	

Materials

eye protection
lab apron
250 mL beaker
watch glass for beaker
10 mL graduated cylinder
two 100 mL graduated cylinders
40 mL of 0.30 mol/L sodium potassium tartrate
40 mL of 3% $H_2O_2(aq)$
5 mL of 0.30 mol/L $CoCl_2(aq)$
hot plate
thermometers or temperature probes

Sodium potassium tartrate, hydrogen peroxide, and cobalt(II) chloride may irritate skin and eyes.

Cobalt(II) chloride is also toxic by ingestion and a possible carcinogen. Handle with care.

Procedure

1. Add 40 mL of 0.30 mol/L sodium potassium tartrate solution to the beaker followed by 40 mL of hydrogen peroxide solution.
2. Heat the solution in the beaker (covered with a watch glass) to 45 °C to 50 °C. Record any evidence of a reaction and of an activated complex.
3. Remove the beaker from the hot plate and add 5 mL of 0.30 mol/L cobalt(II) chloride as a catalyst.
4. Again, cover the beaker with the watch glass and observe the reaction.

Chapter 12 SUMMARY

Outcomes

Knowledge

- analyze and label energy diagrams for a chemical reaction, including reactants, products, enthalpy change, and activation energy (all sections)
- define activation energy as the energy barrier that must be overcome for a chemical reaction to occur (12.1)
- explain the energy changes that occur during chemical reactions referring to bonds breaking and forming and changes in potential and kinetic energy (12.2)
- explain that catalysts increase reaction rates by providing alternative pathways for changes without affecting the net energy involved (12.3)

STS

- recognize the values and limitations of technological products and processes (12.1, 12.3)
- state that a goal of technology is to solve practical problems (12.2)
- evaluate technologies from a variety of perspectives (12.3)

Skills

- initiating and planning: describe procedures for safe handling, storage, and disposal of materials used in the laboratory, with reference to WHMIS and consumer product labelling information (12.3)
- performing and recording: plot chemical potential energy diagrams, enthalpy diagrams, and energy pathway diagrams indicating changes in energy for chemical reactions (all sections);
- analyzing and interpreting: interpret energy diagrams for chemical reactions (all sections)
- communication and teamwork: work collaboratively in addressing problems and apply the skills and conventions of science in communicating information and ideas and in assessing results by using appropriate SI notation, and fundamental and derived units for calculating and communicating enthalpy changes (all sections)

Key Terms

12.1
activation energy, E_a

12.2
bond energy

12.3
catalysis
catalyst
enzyme
intermediate

MAKE a summary

1. Draw a combined potential energy diagram and energy pathway diagram to illustrate the uncatalyzed and catalyzed reaction of hydrogen and fluorine. Add labels and explanations to communicate what you have learned in this chapter, including the concept of catalysis.
2. Refer back to your answers to the Starting Points questions at the beginning of this chapter. How has your thinking changed?

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The following components are available on the Nelson Web site. Follow the links for *Nelson Chemistry Alberta 20–30*.

- an interactive Self Quiz for Chapter 12
- additional Diploma Exam-style Review questions
- Illustrated Glossary
- additional IB-related material

There is more information on the Web site wherever you see the Go icon in this chapter.

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

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Part 1

1. Which of the following statements concerning collision–reaction theory is *false*?
- A. A chemical reaction must involve collisions of reactant entities.
- B. An effective collision requires sufficient energy.
- C. All collisions with the required minimum energy form new bonds.
- D. All collisions without the required minimum energy rebound elastically.

2. Catalysts increase the rate of a chemical reaction by providing a reaction pathway that has
- A. lower activation energy
- B. higher activation energy
- C. lower net energy change
- D. higher net energy change

3. Which of the following statements regarding bond energy is *false*?
- A. Bond energy is the energy released when a bond is formed.
- B. Bond energy is the energy required to break a chemical bond.
- C. The change in enthalpy represents the net effect from breaking and making bonds.
- D. In an endothermic reaction the energy released from bond making is greater than the energy required for bond breaking.

4. The following statements are *not* all true.

NR
1. Catalysts are consumed in the net reaction.
2. Catalysts are not consumed in the net reaction.
3. Catalysts decrease the enthalpy of the products.
4. Catalysts increase the enthalpy of the products.
5. Catalysts decrease the overall rate of a reaction.
6. Catalysts increase the overall rate of a reaction.
7. Catalysts provide an alternate pathway for the reaction.
8. Catalysts are an essential part of most industrial chemical processes.

List, in order, the *true* statements about catalysts.

____ ____ ____ ____.

5. The ignition system in an automobile is designed to provide the engine with
- A. activation energy
- B. enthalpy
- C. oxygen
- D. fuel

6. The catalytic converter in an automobile is designed to
- A. provide more energy
- B. provide more oxygen
- C. improve fuel efficiency
- D. remove nitrogen oxides from the exhaust

7. Which of the following is an example of a catalyst?
- A. enzymes in the production of sugar from starch
- B. ethene in the production of ethylene glycol
- C. heat in the decomposition of water
- D. light in the formation of hydrogen chloride

8. The structural arrangement of entities representing the highest potential energy point in a chemical reaction step is called the
- A. product
- B. catalyst
- C. reactant
- D. activated complex

9. The change in enthalpy of a chemical reaction can be predicted by all the following methods *except*
- A. Hess' law
- B. stoichiometry
- C. bond energies
- D. molar enthalpies of formation

10. All the alkali metals react with water at room temperature to produce hydrogen gas and hydroxide ions. The tendency to react increases as the atomic number of the alkali metal increases. Based on this evidence, which of the alkali metals has the highest activation energy in this reaction?
- A. cesium
- B. lithium
- C. potassium
- D. sodium

Part 2

11. Carbon tetrachloride, $CCl_4(l)$, is a toxic solvent for oils, fats, lacquers, and varnishes. Carbon tetrachloride can be produced by the reaction of methane and chlorine gas.

DE

$$CH_4(g) + 4\ Cl_2(g) \rightarrow CCl_4(l) + 4\ HCl(g)$$

(a) **Describe** the conditions required for a successful collision between methane and chlorine molecules.
(b) **How** would a catalyst change the rate of the reaction?
(c) **Why** does a catalyst have this effect?
(d) **Explain** how bond energies affect the rate of this reaction.
(e) **Explain** how bond energies affect the net energy change of this reaction.

12. Using the concept of bond energies,
(a) **explain** why the oxidation of aluminium is exothermic.
(b) **explain** why the decomposition of aluminium oxide is endothermic.

13. Draw energy pathway diagrams for the following reactions. Label the reactants, products, enthalpy change, activation energy, and activated complex.
(a) $C(s) + O_2(g) \rightarrow CO_2(g) + 393.5\ kJ$
(b) $N_2(g) + 2\ O_2(g) + 66.4\ kJ \rightarrow 2\ NO_2(g)$

14. **Explain** why it is important to avoid producing static electricity while refuelling an automobile.

15. DE Catalytic reforming technology is used to improve the quality of gasoline by converting straight-chain hydrocarbons to aromatic molecules, for example, heptane + energy → methylbenzene + hydrogen (**Figure 1**). **Analyze** this reaction. Your response should include
- a balanced equation including structures
- your justification of which is greater: the energy released from bond making or the energy required for bond breaking
- an energy pathway diagram for the reaction, with labels for the reactants, products, enthalpy change, and activation energy for the catalyzed and uncatalyzed reactions

Figure 1
A catalytic reforming unit

16. Use **Figure 2** to answer the following questions.

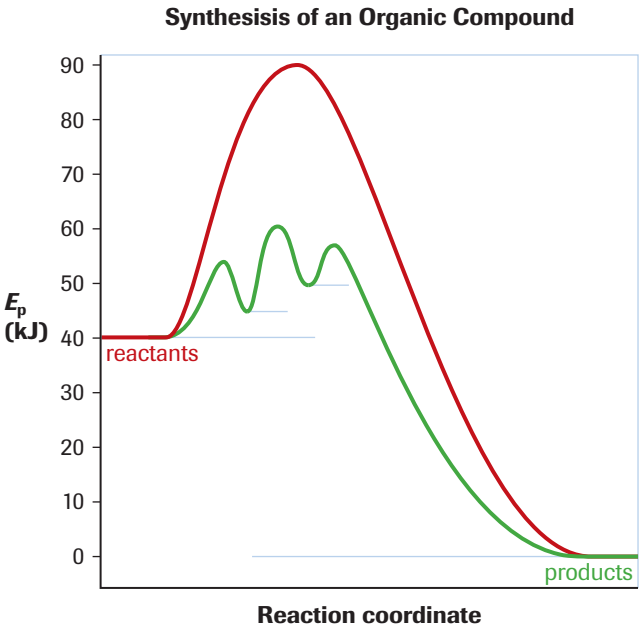

Figure 2
Energy pathway diagram for the synthesis of an organic compound

(a) What is the activation energy for the uncatalyzed forward reaction?
(b) What is the activation energy for the uncatalyzed reverse reaction?
(c) What is the activation energy for the catalyzed forward reaction?
(d) What is the activation energy for the catalyzed reverse reaction?
(e) What is the enthalpy change for the uncatalyzed forward reaction?
(f) What is the enthalpy change for the uncatalyzed reverse reaction?
(g) What is the enthalpy change for the catalyzed forward reaction?
(h) What is the enthalpy change for the catalyzed reverse reaction?

17. **Illustrate** each of the following technological processes with examples. For each example, provide a word equation and suggest a suitable catalyst.
(a) hydrocracking heavy oil to gasoline
(b) pollution control in an automobile catalytic converter
(c) production of high-fructose corn syrup

Many of these questions are in the style of the Diploma Exam. You will find guidance for writing Diploma Exams in Appendix H. Exam study tips and test-taking suggestions are on the Nelson Web site. Science Directing Words used in Diploma Exams are in bold type.

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Part 1

1. The correct units for specific heat capacity are
A. J/(g·°C)
B. kJ/g·°C
C. kg/(J·°C)
D. °C/(g·J)

2. NR Water can be decomposed by electrical energy as shown in the following equation:
$2\,H_2O(l) \rightarrow 2\,H_2(g) + O_2(g) \qquad \Delta_r H° = ?$
The value of $\Delta_r H°$ for the equation as written is _____ kJ (to three digits).

3. NR There are several electrical generating stations in Alberta that use the energy from burning coal to generate electricity. Assuming coal is pure carbon, the temperature increase in 1.00 t of water when it absorbs all the energy produced by the complete combustion of 1.00 kg of coal is calculated to be _____ °C.

Use the following statements to answer questions 4 and 5.

1. Chemical bonds are broken.
2. Chemical bonds are formed.
3. Energy is lost to the surroundings.
4. Energy is gained from the surroundings.
5. The chemical potential energy of the products is less than the enthalpy of the reactants.
6. The chemical potential energy of the products is greater than the enthalpy of the reactants.

4. NR Which statements are true for exothermic reactions?
___, ___, ___, and ___

5. NR Which statements are true for endothermic reactions?
___, ___, ___, and ___

6. The energy barrier that must be overcome in order for a reaction to occur is referred to as the
A. activation energy
B. bond energy
C. enthalpy change
D. molar enthalpy

7. Catalysts are an essential part of most industrial chemical processes. Which of the following statements about catalysts is *false*?
A. Catalysts are not consumed in the net reaction.
B. Catalysts increase the enthalpy of the products.
C. Catalysts increase the overall rate of a reaction.
D. Catalysts provide an alternative pathway for the reaction.

8. Using a catalyst in a chemical reaction
A. increases the enthalpy change of the reaction
B. increases the activation energy of the reaction
C. decreases the enthalpy change of the reaction
D. decreases the activation energy of the reaction

9. NR A chemistry student determines in the laboratory that the molar enthalpy of combustion of methanol is –721 kJ/mol.
$2\,CH_3OH(l) + 3\,O_2(g) \rightarrow 2\,CO_2(g) + 4\,H_2O(g) + \text{energy}$
When the energy term is written as a term in the reaction equation, for the same conditions, the value is

_____ kJ.

10. NR An automobile catalytic converter is a technological invention for the conversion of noxious exhaust gases. For example,
$2\,NO(g) + 2\,CO(g) \rightarrow N_2(g) + 2\,CO_2(g) \qquad \Delta_r H° = ?$

The standard enthalpy change for this reaction is (to three digits).

−_____ kJ.

11. A much studied chemical reaction is communicated by the reaction equation

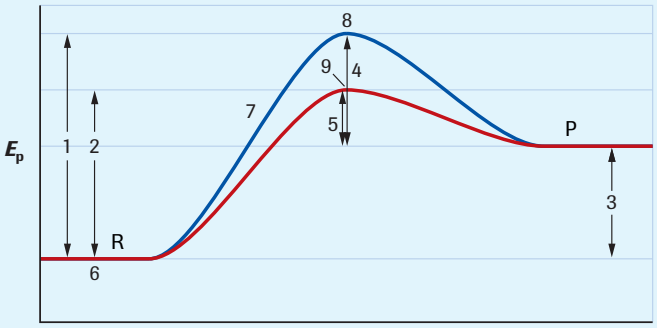
$H_2(g) + I_2(g) \rightarrow 2\,HI(g) \qquad \Delta_r H° = +53.0\text{ kJ}$

This equation is representative of an
A. endothermic formation reaction
B. endothermic decomposition reaction
C. exothermic formation reaction
D. exothermic decomposition reaction

12. Glucose is an important natural product. Which of the following reactions involving glucose is endothermic?
A. Formation of glucose from its elements
B. Combustion of glucose
C. Cellular respiration of glucose
D. Photosynthesis involving glucose

Use this graph to answer questions 13 and 14.

Potential Energy Diagram for System R→P



13. NR Match the appropriate energy change, labelled 1 to 5 in the graph, with the following reactions. Give your answers in the same order as the energy changes listed.

- enthalpy change for the forward reaction
- enthalpy change for the reverse reaction
- activation energy for the uncatalyzed reaction
- activation energy for the catalyzed reaction

___, ___, ___, and ___

14. NR From the graph above, match the appropriate sections, numbered 6 to 9, with the following statements. Give your answers in the same order as the statements.

- the activated complex for the uncatalyzed reaction
- the activated complex for the catalyzed reaction
- the conversion of kinetic energy into potential energy
- the same average chemical potential energy of entities with varying kinetic energy

___, ___, ___, and ___

15. Combustion of a hydrocarbon, cellular respiration, and photosynthesis have much in common. Which of the following is *not* common to all three reactions?

A. energy
B. $CO_2(g)$
C. $H_2O(l)$
D. $H_2O(g)$

16. NR Part of the character of chemicals is their thermal stability. List the following organic compounds in order of increasing stability.

1. sucrose, $C_{12}H_{22}O_{11}(s)$
2. ethanoic acid, $CH_3COOH(l)$
3. ethanol, $C_2H_5OH(l)$
4. glucose, $C_6H_{12}O_6(s)$

___ ___ ___ ___

Part 2

17. **Enumerate** four factors that influence the rate of a chemical reaction.

18. The reaction equation

$A + B \rightarrow C + D \qquad \Delta_r H = -250\ kJ$

represents a hypothetical reaction. **Illustrate** the reaction with an energy pathway diagram showing the catalyzed and uncatalyzed reactions, given that the activation energy is twice as large for the uncatalyzed reaction as for the catalyzed reaction.

19. The reaction between ammonia and hydrogen chloride gas produces a white smoke that was once widely used for "special effects" in dramatic productions.

$NH_3(g) + HCl(g) \rightarrow NH_4Cl(s) \qquad \Delta_r H° = ?$

(a) Use a table of standard molar enthalpies of formation to **predict** the standard enthalpy change for the reaction.
(b) **Predict** which is greater: the energy required for breaking the bonds in the reactant molecules or the energy released by forming bonds in the product. Explain your reasoning.

20. DE The modern method of preparing methanol combines carbon monoxide and hydrogen at high temperature and pressure, in the presence of a catalyst.

$CO(g) + 2\ H_2(g) \rightarrow CH_3OH(l) \qquad \Delta_r H° = ?$

(a) **Explain** the purpose of the catalyst.
(b) **Predict** the standard enthalpy change for the reaction.
(c) **Determine** the quantity of energy released by the production of 1.00 kg of methanol.

21. DE Some of the natural gas fields in Alberta contain hydrogen sulfide, a very poisonous gas. The sulfur is removed by burning some of the hydrogen sulfide to form sulfur dioxide, which is then reacted with the remaining hydrogen sulfide to form elemental sulfur. The overall reaction equation for the process is

$16\ H_2S(g) + 8\ SO_2(g) \rightarrow 16\ H_2O(g) + 3\ S_8(s) \qquad \Delta_r H° = ?$

(a) Use a table of standard molar enthalpies of formation to **predict** the enthalpy change of the above reaction.
(b) **Determine** the standard molar enthalpy of reaction for sulfur, $S_8(s)$.
(c) **Determine** the quantity of energy released by the production of 1.00 t of sulfur, $S_8(s)$.

22. In addition to being a fuel, ethane is used to produce ethene and ethyne, the starting points for the synthesis of a host of useful compounds. Use a table of standard molar enthalpies of formation to **predict** the enthalpy change of the following reactions:

(a) $C_2H_6(g) \rightarrow C_2H_4(g) + H_2(g) \qquad \Delta_r H° = ?$
(b) $C_2H_6(g) \rightarrow C_2H_2(g) + 2\ H_2(g) \qquad \Delta_r H° = ?$

23. Cracking (especially to produce gasoline and ethene) is the most common industrial chemical reaction in Alberta. For catalytic cracking of crude oil fractions into gasoline hydrocarbons, synthetic zeolites (aluminosilicates, $Al_xSi_yO_z$) are the preferred catalysts.

(a) Use the following information (only) to **determine** the enthalpy of cracking for the following reaction:

$C_{10}H_{22}(l) + H_2(g) \rightarrow C_4H_{10}(g) + C_6H_{14}(l)$ $\quad \Delta_{cr}H = ?$

$2\,C_{10}H_{22}(l) + 31\,O_2(g) \rightarrow 20\,CO_2(g) + 22\,H_2O(l)$ $\quad \Delta_cH = -13\,555.8$ kJ

$2\,C_4H_{10}(g) + 13\,O_2(g) \rightarrow 8\,CO_2(g) + 10\,H_2O(l)$ $\quad \Delta_cH = -5\,754.6$ kJ

$2\,C_6H_{14}(l) + 19\,O_2(g) \rightarrow 12\,CO_2(g) + 14\,H_2O(l)$ $\quad \Delta_cH = -8\,325.8$ kJ

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta_cH = -393.5$ kJ

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$ $\quad \Delta_cH = -285.8$ kJ

(b) **Explain** how the addition of the zeolite changes the overall
- (i) enthalpy of reaction
- (ii) rate of reaction
- (iii) activation energy

(c) View an animation of natural and synthetic zeolite.
- (i) What cation is primarily used to enrich the synthetic zeolite to make an even more effective catalyst than the natural crystal?
- (ii) What other cations may be present in the synthetic zeolite catalyst?

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24. Catalysts are one of many technological solutions used to reduce greenhouse gas (GHG) emissions.

(a) List the four GHGs that research shows have the most effect on global warming.

(b) From research, which of carbon dioxide or methane is found to have the larger global warming potential (GWP)?

(c) The catalysts used in catalytic converters in cars are from what class of elements in the periodic table?

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Use this information to answer questions 25 to 27.

The Kyoto Protocol was officially ratified in Canada on February 16, 2005. Canada initially committed to reduce greenhouse gas emissions to 6% below the 1990 level. Part of Canada's initial strategy for reducing greenhouse gases is to have Canadians make a personal commitment to reduce their greenhouse gas (GHG) emissions by 1 t/a. Industry, commerce, and individuals are being challenged to reduce their GHG emissions to help us reach the Canadian target. There is more information on Canada's effort to meet our commitments on the Statistics Canada Web site.

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Table 1 Per Capita Carbon Dioxide Emissions from Fossil Fuel Combustion and Production, 1990 to 2001

Year	Mass of CO_2 emissions (t/a)
1990	15.60
1991	15.04
1992	15.36
1993	15.13
1994	15.45
1995	15.73
1996	15.97
1997	16.22
1998	16.38
1999	16.87
2000	17.50
2001	17.02

Sources: Environment Canada, 2003, *Canada's Greenhouse Gas Inventory, 1990-2001*, Ottawa Statistics Canada, CANSIM, tables 051-0001 and 380-0017 Human Activity and the Environment, Annual Statistics 2004, p. 25, Table 2

25. DE (a) **Table 1** shows the increase in per capita GHG emissions from fossil fuel combustion and production since 1990. What is the percentage increase in this time?

(b) Research recent GHG emissions in Environment Canada's Greenhouse Gas Inventory. Graph the per capita emissions over the last fifteen years or so. Comment on the trends you observe.

(c) What is the Canadian GHG emission target in tonnes per capita? If every one of us meets this target, what will be the percentage reduction in GHG emissions? Relate this to the graph you plotted in (b).

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26. List five ways by which you can personally reduce GHG emissions.

27. **Why** do most Canadians (as indicated by polls) want to reduce the emission of GHGs?

28. At 300 K the activation energy, E_a, for the uncatalyzed DE decomposition of hydrogen peroxide into water and oxygen is empirically determined to be 75.3 kJ/mol. For a particular concentration of the catalyst potassium iodide, also at 300 K, the activation energy is 56.5 kJ/mol.

(a) **Predict** the standard molar enthalpy of decomposition of hydrogen peroxide.

(b) Draw a potential energy diagram, including reaction pathways, to communicate all the information above.

29. **Compare** three different organic fuels, such as methane, DE propane, and butane.

Your response should include

- a calculation of the standard molar enthalpy of combustion for each fuel to produce liquid water
- a calculation of the quantities of energy released per kilogram of fuel
- a calculation of the chemical amounts of carbon dioxide released per kilogram of fuel
- an overall evaluation of the three fuels

30. Ethanoic acid (acetic acid) is an important industrial DE chemical that is manufactured from the reaction of methanol and carbon monoxide using rhodium or iridium catalysts.

(a) Write the balanced chemical equation for the industrial production of ethanoic acid.

(b) **Sketch** a chemical potential energy diagram, and label the enthalpy change.

(c) **Sketch** an energy pathway diagram, and label the activation energies for the uncatalyzed and catalyzed reactions.

(d) Provide the scientific explanation and the technological purpose for using a catalyst.

31. Ethanol can be oxidized (to carbon dioxide and water) in a DE laboratory fume hood through a series of reactions by using a platinum or palladium wire catalyst. Use the reaction mechanism below to answer the questions.

$$CH_3CH_2OH(l) \rightarrow CH_3CHO(l) + H_2(g) \qquad \Delta_r H = +85.3 \text{ kJ}$$

$$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(l) \qquad \Delta H = -285.8 \text{ kJ}$$

$$CH_3CHO(l) + \frac{5}{2} O_2(g) \rightarrow 2\,CO_2(g) + 2\,H_2O(l) \qquad \Delta_r H = -1\,166.3 \text{ kJ}$$

(a) **Determine** the enthalpy change for the overall reaction resulting from the above catalyzed reaction mechanism.

(b) **Explain** how the enthalpy change for the overall reaction is affected by catalyzing the reaction and creating an alternative pathway.

32. Statistics Canada lists the percent hydroelectric power DE generation by province and territory (**Table 2**).

Table 2 Hydroelectric Power Generation by Province and Territory, 1994 and 2002

Province	1994	2002
NL	97.7	93.9
PE	0.0	0.0
NS	10.4	8.5
NB	17.4	12.6
QC	96.5	96.3
ON	25.6	24.9
MB	99.0	97.9
SK	21.9	15.8
AB	3.4	2.8
BC	87.5	90.1
YT	88.9	87.5
NT	32.6	37.9

Note: NT includes NU.
Source: Table B35 on page 80 of HAatE by StatCan

(a) **Analyze** this data (or more recent data from the Statistics Canada Web site) to find any trends and insights concerning the percentage of hydroelectric power generation in Canada.

(b) **Illustrate** the percentage generation of hydroelectric power by province on a bar graph.

(c) **Explain** the difference between hydro use in Alberta and hydro use in one other province or territory.

(d) From an environmental perspective **enumerate** pros and cons for hydroelectric power stations.

(e) If a goal of technology is to provide solutions to practical problems, **evaluate** the solution of replacing fossil fuel power plants with hydroelectric power. Provide at least one pro and one con from at least two perspectives other than environmental.

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33. People living in different regions of Canada use (or in the past have used) different fuels for cooking and for heating their homes. **Enumerate** five different fuels used by peoples in different parts of Canada—north to south and west to east.

34. **Compare** methane and propane as fuels. Establish at least four criteria for evaluating these fuels. Provide quantitative and/or qualitative information for each criterion. Finally, provide a personal choice based upon the information compiled and upon your values. Share your findings as an audio-visual presentation.

35. **Table 3** lists ignition temperatures for various fuels. The DE piloted ignition temperature is the temperature at which the fuel will ignite when provided with a spark or flame (such as a pilot light in a furnace). The spontaneous ignition temperature is the temperature at which the fuel ignites without a spark or flame.

Table 3 Ignition Temperatures

Fuel	Piloted ignition temperature (°C)	Spontaneous ignition temperature (°C)
ammonia[1]	—	651
asphalt	204	485
corn oil	254	393
ethanol	13	390
gasoline	−43	280
methane[1]	—	537
olive oil	225	343
paraffin wax	199	245
propane[1]	—	450
wood	350	600

1 Gas that ignites with a spark or flame at any temperature.
Source:
http://encarta.msn.com/media_461551262/Ignition_Temperatures.html

(a) Use concepts from Chapter 12 to **explain** (theoretically) why gasoline ignites at or above −43 °C when a spark is provided (for example, by a spark plug).
(b) **Explain** where the energy comes from for spontaneous ignition of propane at 450 °C.
(c) Methane ignites with a spark or flame at any temperature. Gas companies advise people to "Call before you dig." What might produce a spark to ignite a broken natural gas line?
(d) Methane, propane, gasoline, and asphalt are hydrocarbons. Consult Table 3 to develop a hypothesis about their relative activation energies. What certainties and uncertainties do you have about the hypothesis you have written?

36. The molar enthalpy of neutralization, $\Delta_n H_m$, for aqueous acid–base reactions can be determined by calorimetry. If one of the reactants is in excess, then the molar enthalpy of neutralization is determined for the other reactant. Complete the Analysis portion of the lab report.

Purpose

The purpose of this exercise it to use calorimetry to determine the molar enthalpy of neutralization for hypoiodous acid when reacted with excess aqueous sodium hydroxide.

Evidence

1.00 L of 0.400 mol/L HIO(aq)
1.00 L of 0.500 mol/L NaOH(aq)
initial temperature of solutions = 21.22 °C
final temperature of mixture = 22.44 °C

37. Over the years there have been many "free energy" devices or "energy machines" advertised on the Internet. The energy output of these devices is claimed to be greater than the energy input. As a skeptic, what kind of authorities would you consult and/or what kinds of tests would you advocate to test these claims?

38. Review the focusing questions on page 474. Using the knowledge you have gained from this unit, briefly **outline** a response to each of these questions.

Extension

39. When investigating reactions to produce ammonia, Haber and Bosch tested some 20 000 candidate catalysts in a trial-and-error process before discovering an iron ore from Sweden that worked well for fertilizer production. (The ore happened to contain traces of alumina and alkali metal compounds.) In the catalyzed reaction of nitrogen and hydrogen, the gases are adsorbed onto the solid iron ore catalyst.
(a) **Compare** the activation energy for the uncatalyzed reaction (red pathway) with the largest activation energy for the catalyzed reaction (green pathway).
(b) **Explain** why the catalyzed reaction is much faster.
(c) **Compare** the enthalpy changes for the catalyzed and uncatalyzed reactions. Comment on the magnitude and sign.

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40. Use a greenhouse gas (GHG) calculator or table of values to see how your energy emissions compare with the national average, and what you can do to reduce your emissions. Determine how you could reduce your GHGs by one tonne per year.

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41. Green chemistry is a term that describes chemical industrial work involving environmental stewardship. Research two examples of green chemistry associated with energy production or use.

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